INDUSTRIAL CHEMISTRY

BEING A SERIES OF VOLUMES GIVING A COMPREHENSIVE SURVEY OF

THE CHEMICAL INDUSTRIES

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RADIATION IN CHEMISTRY

BY

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GENERAL PREFACE

As its title implies, the present series of volumes is intended to cover industrial chemistry rather than chemical technology, and thus to provide a connecting link between text-books on pure chemistry and text-books on chemical technology and chemical engineering. The volumes will be written by chemists and are primarily intended for chemists, but it is hoped that much of the information that they contain will be found useful by the chemical engineer and technologist.

Although the method of treatment must vary to some extent with the different industries, the main theme in each volume will be the chemical structure and chemical properties of the materials employed and manufactured in the branch of industry under consideration, and the chemical reactions which take place during manufacturing operations. Engineering considerations, however, will not be excluded as the necessities of plant construction and considerations of capital cost, corrosion, disposal of effluent, etc., may compel modification of a laboratory process, or may render a chemically less efficient process the more economical one on a manufacturing scale.

Chemistry, pure and applied, is a continually advancing science, and processes which are unknown or are only of scientific interest at present may become of first-class technical importance in a few years or even a few months. For this reason the subject-matter of the volumes will not be confined to those processes which are actually in use at present, but every endeavour will be made to give a brief account of processes which show promise of industrial development in the near future.

A special feature of the series will be a bibliography at the conclusion of each section giving references not only to original literature and patent specifications, but also to larger treatises, and in particular to those in which more engineering and technological detail is to be found.

The industrial chemist should find the volumes of great value for giving a reliable survey of the scientific principles on which his work is based, and for indicating the direction of probable and possible development. In them the chemical engineer will find much information of material assistance to him in the design of plant, and to the advanced student they will be of particular value, not only giving him a survey of the industry he is about to enter, but also by introducing a living interest into his studies by showing how the "pure" chemistry he has learnt in the lecture room and laboratory has been applied to industrial work. Finally, the research worker who wishes to direct his investigations to industrial problems will find numerous themes suggested which can hardly fail to yield results of great practical value.

It is hoped in time to extend the list of volumes so as to cover the whole field of chemical industry, and the Editor will always be pleased to receive suggestions either for new volumes or for extending the usefulness of the present volumes when new editions are called for.

E. DE BARRY BARNETT.

AUTHOR'S PREFACE

THE topics discussed in this volume range over a very wide field, and some explanation of the plan of the work is perhaps necessary.

A natural preoccupation with thermal radiation has tended to obscure the fact that heat is but one of the many forms of energy capable of effecting chemical change. It is true that electrochemical processes are now of great importance, and that photochemistry is at the basis of the photographic industry, but these facts do not disprove the statement that heat remains the great prime-mover of chemical reaction. It is now becoming clear that the technologist may well cast his net with a wider sweep and endeavour to realise how the whole gamut of electromagnetic waves may be pressed into service. We are concerned in this work less with technology than with potentialities for technology, since industrial applications of light and X-rays are still in their infancy. There is no need, however, to stress the fact that the "nascent state" is frequently conducive to a good "yield" in the realms of competitive industry as in chemical reactions.

The most developed branch of our subject is undoubtedly photography. Referring to the technique of making sensitive emulsions, Sheppard remarks that "the methods used in the industry depart considerably from those published." Such a statement, emanating from the Kodak Research Laboratories and backed by Sheppard's authority, is convincing testimony to the futility of concentrating on the purely technological sections of the literature.

A contributor to a series of volumes on Industrial Chemistry has two alternative methods of approaching

his subject; he can either co-ordinate the facts about a specific aspect of Industry and endeavour to see where Chemistry comes in, or, he can marshal his chemical knowledge and find out how and why it may be of use to the technologist. When, however, the important facts about relevant industrial processes are not public property the first method is precluded, and the second method has perforce to be adopted.

I have tried to sift the literature connecting chemical changes with electromagnetic radiations other than heat, and to recount the main facts in such a manner as to throw the industrial aspect into relief. In thus acting as a liaison officer between the armies of pure and applied science, I have not, however, attempted to wear two uniforms at the same time.

Accepting then that I write frankly as a worker in pure chemistry, I have set myself three tasks:

(1) The presentation of an indispensable minimum of theory.

(2) The selection of facts and data of possible value to the technologist.

(3) The discussion of lines of thought and investigation which may have no apparent industrial value, but which seem to provide new and stimulating ways of envisaging the problems of chemists.

I believe that the nature of the subject justifies this treatment.

It must be understood that in certain sections of the book no attempt has been made at a balanced survey of a complete field of investigation. This proviso is especially necessary in the section on vitamins, where the photochemistry of vitamins and not vitamin chemistry in general, is the subject under discussion. In the section on light therapy I have tried to avoid the tendency, which has recently become apparent, to exaggerate the curative value of light. Such excessive optimism is skilfully contested by R. C. Macfie in his excellent "Sunshine and Health" (Home University Library). Actinotherapy opens up great

possibilities for effective co-operation between Chemistry and Medicine, but investigation is much more necessary than propaganda; until we know more than at present, caution is advisable, lest light therapy should suffer a great reaction and fall into the disrepute which overtakes panaceas.

Reading scientific journals is sometimes hard work, but it frequently happens that the lifeless perusal of an apparently dull memoir, is interrupted by a sudden awakening of interest; we realise the boldness of the thought and the refinement of technique which lie behind the work, and a sense of participating in a high endeavour comes over us. We see the researcher shaping a little tile for the mosaic and quietly slipping it into its proper place in the pattern of knowledge. In preparing this volume I have often experienced this lively interest, and it is my hope that, inadequately though I have told the story, I may have awakened sufficient curiosity for the reader to go to the original memoirs as the next best thing if he cannot join in the game himself.

R. A. MORTON.

LIVERPOOL,
February, 1928.

CONTENTS

	PAGE
GENERAL PREFACE	v
AUTHOR'S PREFACE	vii

SECTION I.—LAWS OF PHOTOCHEMISTRY

The nature of radiation, the electromagnetic and quantum theories. The complete spectrum and the different types of radiation. Radiation and matter—reflexion, absorption, and transmission. Lambert's law. Beer's law. The Grotthus-Draper law of photochemical absorption. Types of absorption. The Einstein law of photochemical equivalence. The law of elementary photochemical absorption. The radiation theory of chemical reaction. The validity of the Einstein law. The implications of departures from the Einstein law. Photochemical mechanisms. Activation, predissociational states and molecular phases. Rôle of collisions in activation processes. Views of Plotnikow on the present position of photochemistry. References 1

SECTION II.—LIGHT SOURCES

(*a*) Sunlight, its spectral energy distribution, variations with season, time of day, etc. Light sources depending on the combustion of carbon compounds. Gaslight and gas-mantles. The electric lamp. The Moore tube. Spark and arc sources. Carbon arcs. Mercury vapour lamps of the vacuum and atmospheric types. Metal vapour lamps of other types 15

(*b*) Transparency of materials. Coloured glasses. The manufacture of clear fused quartz. Artificial daylight. Colour-matching pigments. The work of Hill and Howell as an example of methods in this field 34

SECTION III.—MEASUREMENT OF LIGHT INTENSITY

Introductory. Chemical methods a substitute for exact physical measurements. The difficulties in the way of accurate chemical methods. Suggested reactions. The relative

PAGE

merits of a number of tests. The photo-decomposition of hydrogen peroxide. The acetone-methylene blue test. Methods based on the decomposition of oxalic acid in the presence of uranyl salts. The photolysis of potassium nitrate. The photo-decomposition of carbon tetrachloride. The response of the different reactions to various regions in the visible and ultra-violet regions. The deterioration of quartz-mercury vapour lamps followed by actinometric methods 50

SECTION IV.—PHOTOCHEMICAL REACTIONS

(*a*) Photochemistry of water and hydrogen peroxide. Photochemical combination of hydrogen and oxygen. Decomposition of water. Synthesis of hydrogen peroxide. Decomposition of hydrogen peroxide. Action of added substances in retarding or accelerating the decomposition of the peroxide 70

(*b*) The oxygen-ozone system. Formation of ozone. Selective absorption by ozone. Decomposition of ozone in the ultra-violet and in the visible. Action of inert gases . . 74

(*c*) The reduction of carbon dioxide. Photosynthetic possibilities. The resemblance between the silent electric discharge and ultra-violet radiation. Rôle of moisture. The formaldehyde question. The photo-polymerisation of formaldehyde with formation of sugars and other substances. Surface reactions and photosynthesis 77

(*d*) The action of light on organic compounds in general. General. Photo-polymerisation especially of anthracene, vinyl derivatives, etc. Photochemical decompositions with special reference to glycerol, acetone, oxalic acid, sugars, starch, and cellulose. Photochemical synthesis, taking as examples anilides, vanillin, and formhydroxamic acid. Photochemical rearrangements 91

(*e*) Applications of photochemical changes. Fading of dyestuffs. Quick-ageing tests. Rubber. Lithopone. Oils. Filters for obtaining monochromatic light 103

(*f*) Photo-halogenation 113

SECTION V.—THE PHOTOGRAPHIC AND ALLIED INDUSTRIES

The processes involved in photography. Silver halides. Theories of the latent image. The "silver-body" and the "bromide-body." The visible and latent images. Gelatin "X," and complex sulphur-containing compounds. Spectral sen-

PAGE

sitivity. Sensitisation and theories of orthochromatic and panchromatic photography. Sensitisers and desensitisers. Photography in the extreme ultra-violet. Photographic emulsions and colloid chemistry. Grain size. Ripening. The "characteristic curve." Development. Exposure meters. Photography and printing. Bichromated colloids. Colour printing. Colour photography. The platinotype process 125

SECTION VI.—PHOTO-ELECTRICITY AND LUMINESCENCE

Selenium and thalofide cells. Mechanism of the change in resistance. The photo-electric effect and the main facts concerning the experiments under different conditions. The Einstein equation. The relation between the photo-electric effect and chemical properties. Applications to photometry. Phonofilms. Photo-voltaic cells. Phosphorescence. Stokes' law. Work of Lenard and Klatt. Preparation of phosphors. The theory of luminescence. Baly's views. Applications of sulphide phosphors. A brief note on the commercial production of radium and on the therapeutic and other applications of radium 158

SECTION VII.—BIOCHEMISTRY AND LIGHT

(*a*) General. The eye, its protection from ultra-violet rays and the reasons for such measures as are needed. The process of vision, rôle of rhodopsin or visual purple, and the bleaching process. Photosensory process in the clam *Mya arenaria* and in *Volvox globator*. Animal luminescence. Efficiency of the process. Luminous organs and luminous bacteria. The luciferin-luciferase-oxygen system. The reduction of oxyluciferin. Possibilities with chemi-luminescence and animal luminescence contrasted, as involving principles applicable to lighting. Action of light on proteins, blood enzymes, etc. 186

(*b*) Photo-sterilisation. Delimitation to a definite range of wave-lengths. Distinction between stimulative and bactericidal rays. Correlation of the absorption spectra of aromatic amino-acids and the bactericidal rays. Action of light on different types of bacteria. Limitations of photo-sterilisation. Applications, patents, and methods generally for utilising the bactericidal property. Milk. Large scale sterilisation of water 195

PAGE

(c) Light therapy. Finsen's pioneer work. Rollier's sun-cure for surgical tuberculosis. The quartz-mercury vapour lamp and electric arcs in therapeutics. Erythema as a guide to dosage 202

(d) Vitamins and light. The differentiation between vitamins A and D. Rickets, cod-liver oil and ultra-violet light. The acquisition of anti-rachitic potency on irradiating foods. The chemical separation of cod-liver oil into its constituents and the information thereby obtained as to the properties of vitamins A and D. Irradiation of cholesterol. Detection and concentration of an "X" substance using the spectroscope for control purposes. A physical criterion for provitamin-D. Identity of the "X" substance with ergosterol. The irradiation of ergosterol. The occurrence of ergosterol in vegetable oils. The spectroscopic assay. Vitamin-D and calcium metabolism. Experiments on farm stock. Commercial possibilities 206

SECTION VIII.—X-RAYS IN CHEMICAL THEORY AND PRACTICE

Gas tubes and vacuum tubes. The nature of X-rays. Läue, Friedrich, and Knipping's decisive investigations. Bragg's spectrometer. Methods of crystal analysis. The powder method. The interpretation of X-ray data. The allotropy of iron. The iron-carbon system. The system copper-aluminium. Binary alloys. Cold working of metals. Cellulose. Rubber. The stretching of rubber. X-rays and medicine. Penetration of X-rays into metals, etc. Detection of flaws. X-rays and old masters. X-rays and new elements 228

APPENDICES

I. Electrostatic Precipitation 267

II. The Investigation of Absorption Spectra . . . 271

III. Constants Concerning Radiation and Chemistry . 272

Name Index 273

Subject Index 279

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Photography as a Scientific Implement. A Collective Work. (Blackie and Son, Ltd.) 1923.

Practical Applications of X-rays. By G. W. C. Kaye. (Chapman and Hall, Ltd.) 1922.

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AGRICULTURAL ... BATORE

RADIATION IN CHEMISTRY

Section I.—THE LAWS OF PHOTO-CHEMISTRY

Radiation is the transference of energy by means of vibrations propagated in the ether at a velocity of 3×10^{10} cm. per sec. Two apparently divergent theories as to the nature of radiation hold the field. The electromagnetic theory of Faraday and Maxwell regards the vibrations as oscillatory changes of electric charge and magnetic induction, the electric vector being perpendicular to the magnetic vector, and both being perpendicular to the direction of propagation. This theory requires continuity in the emission of energy. Planck and others have proved the necessity for discontinuous emission of energy if many phenomena are to receive a rational explanation. Modern sub-atomics requires that radiant energy should be propagated in empty space in discrete, undivided "quanta," and that any atomic resonator must absorb a whole quantum or none. The "quantum" is a compact bundle of energy of magnitude $h\nu$ where h is a universal constant known as Planck's Constant and is equal to $6{\cdot}554 \times 10^{-27}$ ergs sec. Whilst the continuous wave theory has still to be used in explaining the phenomena of diffraction and interference (although recent developments indicate that a modified quantum treatment is possible even here), for a tremendous field of physical research the quantum theory has assumed undisputed sway. In chemistry, quantum considerations are becoming increasingly important.

The property which differentiates one kind of electro-

magnetic radiation from another is that of wave-length (λ). This, or its reciprocal, the wave-number, or the frequency ν where ν is the velocity of light divided by the wave-length, at once serves to fix the type of radiation.

The following units of wave-length are in use :

Micron μ	=	10^{-3} mm.
*Millimicron $\mu\mu$	=	10^{-6} mm.
Ångstrom unit Å.	=	10^{-7} mm.

e.g. visible light extends in wave-length from
0·0000038 (violet) to 0·000078 cm. (red) ;

or	0·38μ	to	0·78μ
or	380$\mu\mu$	to	780$\mu\mu$
or	3,800 Å.	to	7,800 Å.

Chart of Electromagnetic Wave Spectra.

Type.	Wave-length.	Detection.
Penetrating height radiation ..	0·002 approx. $\mu\mu$	Ionisation, etc.
Gamma rays from radium, etc.	0·002$\mu\mu$–0·137$\mu\mu$	
X-rays	0·007$\mu\mu$–1·32$\mu\mu$	Crystal reflection.
Extreme ultra-violet	20$\mu\mu$–120$\mu\mu$	Vacuum grating spectrograph.
Schumann region	120$\mu\mu$–185$\mu\mu$	Fluorite spectrograph (vacuum).
Short-wave ultra-violet ..	150$\mu\mu$–220$\mu\mu$	Ditto.
Middle ultra-violet	220$\mu\mu$–300$\mu\mu$	Quartz spectrograph.
Near ultra-violet	300$\mu\mu$–390$\mu\mu$	Ditto.
Visible	390–450$\mu\mu$ violet 450–490$\mu\mu$ indigo 490–530$\mu\mu$ blue 530–560$\mu\mu$ green 560–600$\mu\mu$ yellow 600–650$\mu\mu$ orange 650–800$\mu\mu$ red	
Short-wave infra-red	800–1,000$\mu\mu$ 1μ–16μ	Rock-salt spectrograph, thermopile, etc.
Long-wave infra-red	16μ–300μ	
Reststrahlen	300μ–1,000μ	
Electric waves	0·1–1 cm.	Little investigated.
Shortest Hertzian waves ..	2 mm.–10 m.	
Wireless waves	50 m.–20 Km.	
Alternating current supply ..	up to 6,000 Km.	

The whole range covers upwards of fifty octaves, and the methods of generating and using the various types of radiation have wide implications for chemistry.

The law of conservation of energy demands that the radiant energy incident on any surface must be quanti-

* mμ is often used instead of $\mu\mu$.

tatively accounted for by three factors—reflection, absorption, and transmission.

In passing through layers of equal thickness of a homogeneous material equal fractions of the incident radiant energy are absorbed (Lambert's Law). (This is true for monochromatic radiation, but not necessarily true for the total absorption of radiant energy of many wave-lengths or of an extended range of wave-lengths.) In other words, as the thickness traversed increases in an arithmetical ratio, the light or radiation transmitted decreases in a geometrical ratio, or if I_0 is the intensity of radiation of a given wave-length entering a layer δd :

$$-\delta I/\delta d = KI,$$

integrating $$I = I_0 e^{-Kd}$$

in which I_0 is the original intensity,

I is the intensity transmitted through a thickness d, and

K is a constant characteristic of the absorption of a specified material for radiation of specified wave-length.

This suggests that the absorption of radiation is a molecular effect. It would therefore follow that solutions in transparent solvents should obey Beer's Law, which simply requires the absorption to be independent of dilution so long as the total number of solute molecules in the path of the light is maintained constant by suitably increasing the length of tube, *e.g.* the absorption of radiation of wave-length λ by 1 cm. of N solution should be the same as that of 1 mm. of 10 N solution and 10 cm. of N/10 solution.

The Grotthus-Draper Law of photochemical absorption states that only radiations of those wave-lengths which are absorbed can produce photochemical changes. The radiant energy absorbed is given by

$$I_0(1 - e^{-kcd})$$

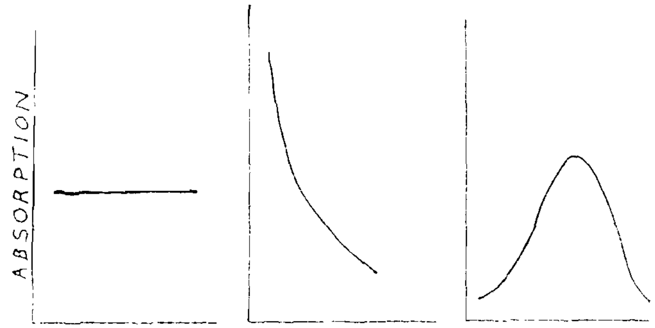
c = concentration of material,
d = total thickness,
k = absorption constant.
($kc = K$ of preceding paragraph.)

for any particular wave-length. The rate of photochemical change should therefore be proportional to the rate at which radiant energy is absorbed, hence $dc/dt = pI_0(1 - e^{-kcd})$ with p a constant. The correlation of chemical change with absorption of radiation is complicated by the fact that the use of monochromatic light is rarely practicable on account of the low intensity which results from the exclusion of other rays. Generally, the absorption and its effects must be considered over a fairly extended range of wave-lengths.

It is customary to express the absorption by means of a curve in which the extinction coefficient is plotted against wave-length, the former being defined from the relation

$\log I_0/I = ecd$, which follows from Lambert's Law.

e = molecular extinction coefficient,
c = concentration in gram-moles per litre,
d = thickness in centimetres.
c is, of course, left out for solids.
These curves are of three types :



Uniform absorption. General absorption. Selective absorption.

FIG. 1.

It will be realised at once that in the interaction between matter and radiation the absorption spectrum must form the basis of our explanations.

The Grotthus-Draper Law received a new formulation in terms of the Einstein Law of Photochemical Equivalence. This law postulates that each single molecule requires one quantum of energy ($h\nu$ at the right frequency) for decomposition by radiation to occur.

Restating the conception, the photochemical decomposition of a gram-equivalent of a substance requires radiant energy equal in amount to N$h\nu$, when

N is the number of molecules per gram-molecule,

h is Planck's constant,

ν is the frequency of the active radiation.

The whole subject of the mechanism of chemical reaction is still in a very controversial state, and the range of validity of the Einstein Law is not yet decided.

Henri and Wurmser [1] extend the connection between the absorption spectrum and photochemical reaction in a very precise way in their *Law of Elementary Photochemical Absorption*, which is confirmatory to the Grotthus-Draper Law. "The photochemical susceptibility of a substance depends only on that part of the absorption spectrum which corresponds with the same molecular groupings as those on which the action is produced."

In order to explain the temperature coefficient of chemical reactions Arrhenius assumed that only those molecules associated with a certain minimum amount of energy were capable of undergoing chemical change. The existence of these "activated" molecules is by now generally accepted, and the basis of contention has been shifted to the mechanism of the activation process. One very important school of thought, in which Trautz,[2] W. C. McC. Lewis,[3] and Perrin [4] have been prominent, suggests that just as in a purely photochemical reaction the absorption of radiation causes the activation, so in a thermal reaction activation must be due to the thermal radiation which is present at all temperatures. Perrin argued that if the specific rate of a unimolecular gas reaction is constant even at very low pressures, activation must occur by means of radiation, since the opportunities for activation by the alternative method of collisions must continually decrease as the pressure is lowered. The clearest case of a unimolecular gas reaction—the decomposition of nitrogen pentoxide—does, in fact, show a velocity independent of pressure over a very wide range.

Unfortunately for the radiation theory, the thermal radiation is not present in sufficient amount to account for the high rate of decomposition of the pentoxide. Lewis and Smith [5] argued that the theory could only be retained if the gas showed a very high coefficient of absorption over a considerable portion of the infra-red region of the spectrum. Daniels [6] showed that absorption on such a scale was not observed between the visible and 8μ. Accordingly it was necessary to carry the investigation still further into the infra-red. Lewis and Mayer [7] therefore attempted to make an investigation over the whole important spectral range.

" At long wave-lengths such a study is extremely difficult. But by dispensing entirely with windows, using a black body at 100° C. and 200° C. as the source of radiation, using a thermopile, as sensitive as it can be made without enclosing it in a vacuum, to receive the radiation, and by placing between the radiation and the thermopile a vessel through which pure dry air, or air mixed with nitrogen pentoxide, could be passed, we were able to obtain rough measurements of the coefficient of total absorption. This proved to be of the same order of the magnitude, and certainly not much larger than the absorption coefficient at the longest wave-lengths investigated by Daniels.

" As far, therefore, as these rough measurements went they seemed to disprove the hypothesis that the decomposition of nitrogen pentoxide is activated by radiation."

It had previously been found by Daniels that external radiation had little or no effect on the decomposition of nitrogen pentoxide. As Lewis and Mayer point out, all experiments of this sort are open to the criticism that the effective portion of the radiation may be largely absorbed before it has penetrated far into the gas, and also that deactivation of partially activated molecules by collisions of the second kind (inelastic collisions) takes place so rapidly at normal pressures that the increase in specific rate cannot be distinguished from that due to the general temperature

rise of the gas. In order to avoid such criticism, it was decided to study the reaction of a molecular stream passing through an exhausted enclosure which is permeated by radiation corresponding to a temperature that would be sufficient under ordinary circumstances to produce chemical reaction. In the molecular stream the gas is at so low a pressure that the mean free path is considerably longer than the stream, and consequently the number of collisions is so small that the reaction may safely be regarded as due to radiation alone.

This plan was realised experimentally very recently by the investigation of the racemisation of pinene, a reaction which has been shown by Smith[23] to be unimolecular. Judged from the temperature coefficient of the reaction, the racemisation should have proceeded at the very least to the extent of 10 per cent. under the experimental conditions, whereas not the slightest change was detected.

The radiation hypothesis is therefore definitely inapplicable to this particular reaction. Recent work by Hinshelwood and Thompson,[8] Hinshelwood,[9] and Ramsperger[10, 11] and Rice, shows that the typical unimolecular reaction does suffer a diminution in reaction rate with a lowering of the pressure, so that the theory of activation by radiation appears to have little support.

In an important paper on "radiation and collision in gaseous chemical reactions," Hibben[12] has found that the decomposition of nitrous oxide and of ozone is unaffected by infra-red radiation. This author goes on to say that the remaining postulate, activation by collision, has been the subject of considerable speculation. "Simple activation by collision has been found adequate to account for the bimolecular decomposition of nitrous oxide, hydrogen iodide, chlorine monoxide, acetaldehyde, and the formation of hydrogen iodide, but when applied to unimolecular reactions is wholly inadequate." Although various general and specific suggestions have been made, it seems clear that "activation by collision alone will not always maintain an undiminished concentration of active molecules as required."

There is no need to carry the discussion of the various suggestions any further in this place, as we are only concerned with the rôle of radiation in chemical reaction. It only remains to say that with the radiation and collision theories being both inadequate, we are left without any satisfactory mechanism for the vast majority of chemical changes.

We may now discuss the validity of the Einstein Law of Photochemical Equivalence, which must, of course, be restricted to purely photochemical changes. Stark, who proposed the relation—energy absorbed per mol, $Ne=Nh\nu$, before the appearance of Einstein's views, emphasised the necessity for restricting the argument to the primary product of photochemical change. A definite step forward was taken by Warburg, who initiated a series of masterly investigations designed to test the validity of the law of photochemical equivalence (1912–1921), and some of the terms which he used must be quoted.

(*a*) *The fundamental photochemical-equivalent* p is the number of gram-mols required for the absorption of one gram-calorie of radiant energy of frequency ν, and consequently the number of gram-mols primarily decomposing per absorbed gram-calorie,

$$i.e.\ p=\frac{4{\cdot}186\times 10^{7}}{N.h.\nu}=\frac{\lambda}{28470}\ \text{mols.}$$

(λ microns; $h=6{\cdot}554\times 10^{-27}$; $N=6{\cdot}062\times 10^{23}$).

(*b*) *The specific* (*effective*) *photochemical equivalent* Φ is an experimental quantity of the same dimensions (mols per absorbed calorie) and expresses the final result of the photochemical reaction, including primary, secondary, or partial reactions. The term effective photochemical equivalent refers to the number of *absorbing* gram-molecules *actually* decomposed per absorbed calorie, whilst the term *specific* photochemical equivalent may refer either to mols of absorbing reactant (disappeared) or of resultant (produced). The quantum efficiency given by γ,

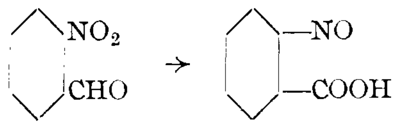
$$\gamma=\Phi/p$$

represents the number of absorbing molecules which have reacted per absorbed quantum.

It is therefore the ratio of the *effective* to the fundamental photochemical equivalent, and becomes unity if the Einstein Law holds.

The experimental data available in which the law is valid include the following:

(1)



o-Nitrobenzaldehyde→o-Nitrosobenzoic acid (Weigert and Brodmann,[13] in which $\gamma=0{\cdot}5$. Reasons are given why the constant should be 0·5 instead of 1·0).

(2) $3O_2 \rightarrow 2O_3$ (Bodenstein [14]), $\gamma=1$.

(3) $2O_3+Cl_2 \rightarrow 3O_2+Cl_2$, $\gamma=1$.

(4) Decomposition of gaseous hydrogen iodide and hydrogen bromide (Warburg, 1916, 1918), $\gamma=2$.

(5) Decomposition of Cl_2O in carbon tetrachloride (Bowen [15]), $\gamma=0{\cdot}83-1{\cdot}02$.

(6) The bromination of cyclohexane $Br_2+C_6H_{12} \rightarrow C_6H_{11}Br+HBr$ (Noddack [16]), $\gamma=1$.

(7) The chlorination of trichlormethane (Noddack), $\gamma=1$.

(8) Ozonisation of oxygen (Warburg [17]), $\gamma=0{\cdot}96$ at $207\mu\mu$.

(9) Among other reactions which have been found to obey the law are the photolysis of ketones, aldehydes, and aliphatic acids; the decomposition of uranyl formate and oxalate, and of chlorine monoxide (Cl_2O) and chlorine dioxide (ClO_2) in the gaseous state and in carbon tetrachloride solution.

The oxidation of ferrous ions by iodine and the hydrolysis of chloracetic acid have also been quoted as in conformity with the law, as also have the reactions

$$2CCl_3Br+Cl_2 \xrightarrow{\text{light}} 2CCl_4+Br_2$$
$$2CCl_3Br+O_2 \longrightarrow 2COCl_2+Br_2+Cl_2.$$ Cf. Grüss.[18]

The o-nitrobenzaldehyde→nitrosobenzoic acid reaction may

be carried out in the solid state and the quantum efficiency is found to be about 1. In the photochemical decomposition of silver bromide and of silver chloride $\gamma=1$ for the initial stages of the reactions.

On the other hand, very low and very high values for the quantum efficiency are not uncommon. The former class includes the decomposition of solutions of potassium nitrate and potassium permanganate, the reversible change of maleic and fumaric acids in aqueous solutions, the hydrolysis of the chlorplatinic acids by light of long wave-length, and other reactions.

The group of reactions showing high values for γ includes the decomposition of the following: aqueous hydrogen peroxide, dilute solutions of uranyl oxalate, and the ferric salts of organic acids. Many reactions involving the halogens show high γ values. Most photochemical reactions occur more readily with short-wave light than would be expected from the Einstein equation, so that the expression is not in conformity with experience so far as the effect of the wave-length of the active light is concerned.

The failure of the "law" implies that secondary effects are overwhelmingly important in determining the course of most photochemical reactions, and that the primary process itself need not necessarily be in conformity with the simple theory. No photochemical reaction can be regarded as elucidated until, as Winther says,

(*a*) The absolute energy values of the incident radiation,

(*b*) The extinction coefficients of the absorbing system for all wave-lengths used, and

(*c*) The velocity of reaction of the purely photochemical process for different values of radiation and wave-length have all been evaluated.

The unsatisfactory position of the fundamental laws of photochemistry may be gauged from the views of so distinguished an authority as Plotnikow,[19] who expressed himself in the following terms:

"Einstein's so-called law of photochemical equivalence in its hitherto accepted form must be dropped as altogether

mistaken. On the other hand, the experience based on the quantum theory must be utilised as a basis for extension and elaboration of the Grotthus-van't Hoff fundamental law."

An interesting attempt has been made by Lasareff [20] to account for the failure of the Einstein relation. The absorbing system is regarded as an equilibrium mixture of molecules in different Bohr states, some having more and some having less energy. Every molecule must have a certain minimum energy content before it can undergo chemical change. The degree of conformity with the Einstein Law will depend on the magnitude of the minimum energy content and the statistical distribution of the absorbing molecules in the different molecular "phases." This idea has been expressed by Baly [21] in a series of papers on absorption spectra.

It must, however, be stated that the law of photochemical equivalence cannot be dismissed very easily. There can be little doubt that the absorption of a quantum of light results in molecular excitation, and that *for this process the law is obeyed.* Excited molecules probably have a mean life of the order of 10^{-7}—10^{-8} sec., and chemical reaction is only one of several alternative processes which may occur. The exact rôles of fluorescence, of collisions, and of intramolecular vibrations are not yet clear. For these reasons it seems wise to retain the idea of photochemical equivalence and to seek for an explanation of its failures in terms of the mechanism of reactions.

Photochemical Mechanisms.—The mechanism of photochemical change cannot be elucidated without a definite advance in the interpretation of absorption spectra. The two leading investigators in this field, Baly and Henri, agree in interpreting light absorption in terms of the quantum theory, Baly considering that the absorption of a quantum of light raises the molecule to a higher energy level. The molecules existing on different energy levels are described as molecular phases, and each is characterised by a different absorption band. Reactivity depends on raising the absorbing molecule to a critical energy level. Henri has

proved quite definitely the existence of "predissociational" states akin to Baly's "molecular phases." We may venture to say that the true interpretation of absorption spectra will be on the general lines laid down by these workers, and that a trustworthy means of analysing the data of absorption spectra will involve the rejection of many suggested photochemical mechanisms. It must be emphasised that the absorption of a quantum of energy greater in amount than the energy required for dissociation *need not necessarily* result in the dissociation process. Mechanisms such as

$$O_2 \rightarrow 2O \qquad \text{(in the formation of ozone)}$$
$$HBr \rightarrow H+Br$$
$$Cl_2 \rightarrow 2Cl$$

are probably untrue.

Stern and Volmer [22] proved in the case of the fluorescence of iodine vapour that a molecule could absorb and re-emit quanta much larger than that corresponding with the energy of dissociation *without decomposition occurring*.

The primary product of light action is almost invariably an activated molecule with an electron in a higher quantum state. (Baly's molecular phase.) Collision of one kind or another will then determine reactivity, *e.g.* the hydrogen-chlorine reaction may follow from:

$$Cl_2 + \text{quantum} \rightarrow Cl'_2 \text{ (activated)}$$
$$Cl'_2 + Cl_2 \rightarrow Cl_2 + 2Cl$$

The importance of collisions has been widely recognised owing largely to the work of Born and Franck.[12] Many investigators regard activation as consisting of a loosening or partial separation of valency electrons, in other words a predissociation process. The activated molecules are unstable and tend to give up their energy of activation very readily. With few exceptions the life of the activated molecule is of the order 10^{-7} to 10^{-8} sec., and the energy is lost either by collisions or in the process of fluorescence.

The collisions may be effective chemically or they may simply result in degradation of energy.

The rôle played by collisions has been partly elucidated by Franck and his colleagues, and as a result the following mechanisms are regarded favourably :

$$Cl_2 + h\nu \rightarrow Cl'_2$$
$$Cl'_2 + O_2 \rightarrow Cl_2 + O'_2$$
$$O'_2 + 2H_2 \rightarrow 2H_2O$$

or

$$Cl_2 + h\nu \rightarrow Cl'_2$$
$$Cl'_2 + Cl_2 \rightarrow 2Cl + Cl_2$$

or

$$NOCl + h\nu \rightarrow NOCl'$$
$$NOCl' + NOCl \rightarrow NO + Cl + NOCl$$

or

$$Cl'_2 + SO_2Cl_2 \rightarrow Cl_2 + SO_2 + Cl_2$$

A most striking example is the dissociation of hydrogen in the presence of mercury vapour illuminated by short-wave ultra-violet light.

$$Hg + h\nu \rightarrow Hg'$$
$$Hg' + H_2 \rightarrow Hg + 2H. \quad \text{(See 70.)}$$

The foregoing ideas on photochemical mechanism do not, however, throw much light on reactions exhibiting high quantum efficiencies. These changes are invariably exothermic, and the fate of the liberated radiation is not quite clear. Most of the reactions are now explained by chain mechanisms such as the interesting but probably inaccurate scheme suggested by Nernst :

$$Cl_2 + h\nu \rightarrow 2Cl$$
$$Cl + H_2 \rightarrow HCl + H$$
$$H + Cl_2 \rightarrow HCl + Cl$$
$$2Cl \rightarrow Cl_2$$
$$2H \rightarrow H_2$$

and the truer chain :

$$Hg' + H_2 \rightarrow 2H + Hg$$
$$H + C_2H_4 \rightarrow C_2H_5$$
$$C_2H_5 + H_2 \rightarrow C_2H_6 + H$$
$$2H \rightarrow H_2$$

Chain mechanisms must play a great part in some of these reactions, but convincing proof for any particular hypothesis seems at present to be difficult of attainment.

In concluding this preliminary survey some very apt remarks of Plotnikow may be quoted.

" The development of every scientific study may be

divided into three phases—the first, the chaotic, in which an accumulation of experimental data takes place, and confusion of opinion prevails; the second, that of the establishment of its fundamental laws, and the classification and systemisation of the experimental material; and the third, which is the normal progress of the science as such, accompanied by its vigorous development in its applied form. Photochemistry is at present in the second stage, which, as a matter of fact, always represents a turning point in the history of a given branch of science."

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SECTION II.—LIGHT SOURCES

I. SUNLIGHT

THE available energy of the world is almost entirely traceable to sunlight. The body of the sun consists of a white hot (5,000°–7,000°) radiating surface called the photosphere, which is surrounded by an envelope of vapours of rather lower temperature, called the chromosphere. The light emitted by the photosphere is continuous in character, but the spectrum as we observe it consists of a continuous background crossed by a very large number of fine dark lines

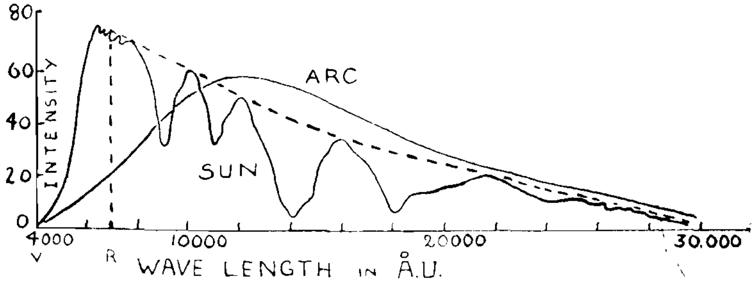


FIG. 2.—(After Langley.)

(Fraunhöfer lines), due to the absorption of light by elements existing in the chromosphere. The spectrum of sunlight as it reaches the earth extends from 2,960 Å.U. to 30,000 Å.U., if we neglect the very low intensity rays on either side of these limits.

Sunlight thus contains ultra-violet rays extending from $290\mu\mu$ to $380\mu\mu$, approximately from $380\mu\mu$ to $780\mu\mu$ of visible light and from $0{\cdot}78\mu$ to $3{\cdot}0\mu$ of infra-red rays of fairly high intensity. The position of maximum energy occurs within the visible spectrum.

In Fig. 2 (after Langley) the spectral distribution of

solar energy is given by the irregular curve. The depressions are due to the absorption of radiation either by the sun's chromosphere or the earth's atmosphere. The true curve would if these disturbing factors were absent probably follow the dotted line.

It will be seen that the spectral distribution of energy in the light from an electric arc (or incandescent filament) lamp shows a smooth curve with its maximum shifted into the short-wave infra-red region.

"Daylight" is an ambiguous term, since it varies in its spectral intensity distribution.

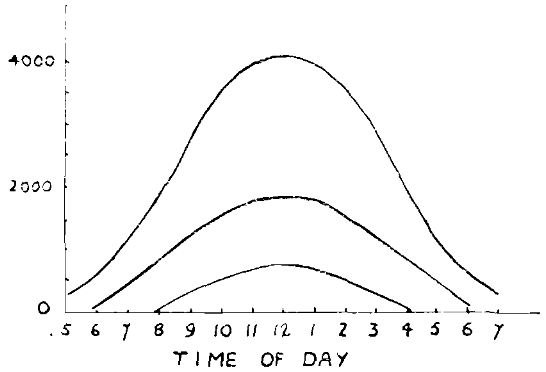


FIG. 3.—Daily variation of illumination at Midsummer, Equinox, and Midwinter.

The following table from Walsh's *Lighting and Photometry* shows the relative compositions of daylight and some artificial light sources.

	Red.	Green.	Blue.
Noonday sunlight (taken as)	100	100	100
North blue skylight ..	78	82	140
Tungsten vacuum lamp ..	183	96	21
Tungsten gas-filled lamp ..	164	102	34

The balance may be redressed in artificial light sources by colour screens, which reduce the intensity of the red light.

At the present time a great deal of interest is being displayed in the ultra-violet portion of the solar spectrum, since rays in this region seem to play an important part in health and disease. For instance, rickets in the North

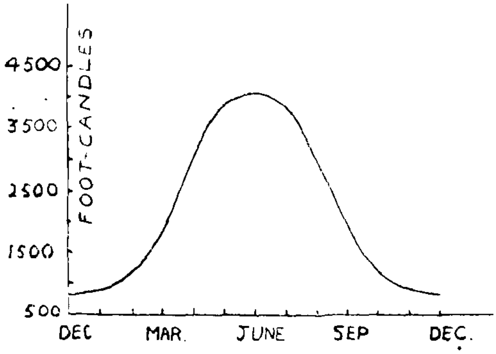
Temperate Zone is commonly found to be a disease of late winter and spring; its incidence spontaneously decreases in summer, a phenomenon which has been connected with seasonal variations in sunlight. One observer records the following limiting wave-lengths of ultra-violet solar radiation detectable by ordinary means:

December to February	3,120 Å.U.
September to November	3,080 Å.U.
March to May	3,010 Å.U.
June to August..	2,962 Å.U.

On an arbitrary scale the relative intensities of radiation are given as follows:

January	100 units.
April	400 ,,
July	1,000 ,,
October	600 ,,

An important issue is raised by these results. Industrial civilisation brings in its train pollution of the air by smoke,



VARIATION OF NOON SKYLIGHT

FIG. 4.

dirt, and gaseous products, which between them act as a very efficient screen for reducing the intensity of the beneficent ultra-violet solar radiation.

Perhaps the principal means of utilising the energy of sunlight consists in the photosynthesis practised by living plants. The active rays appear to be those absorbed by the green plant pigment, chlorophyll, and it is striking that

photosynthesis should utilise those rays which are most intense in the solar spectrum. Terrestrial life depends for its continuance on the photochemical processes occurring in the living plant. At present these are so little understood, in spite of brilliant onslaughts into the problem of their nature, that the study of phytosynthesis has resulted in little of technical value. As soon, however, as a trustworthy explanation can be found for the photo-catalysis which occurs in the leaf, applied photochemistry may be expected to undergo profound changes.

2. Artificial Light

Light sources used in air may be classified as follows:

(*a*) Those depending on the incandescence of particles of carbon or other materials.

(*b*) Those depending on the principle of the electric arc or spark.

When candles or oil lamps are used, the light evolved is due to incomplete combustion, which results in the formation of tiny particles of carbon which are raised to incandescence in the flame. The efficacy of these illuminants depends to a great extent on the capacity possessed by the eye for adjusting itself to low intensities of light. In the ordinary photochemical sense these light sources are extremely inefficient. The lime-light and the incandescent gas-mantle are certainly much better, but are both now becoming obsolete.

Oil-burning (paraffin) lamps have been improved in two ways:

(1) The use of a glass chimney causes an upward draught and thus favours more complete combustion. (2) More efficient burners cause a better regulation of the flame size.

A more definite advance occurred with the advent of the paraffin vapour lamp. The oil is vapourised by its own heat of combustion in a special chamber, and once the lamp is running properly the vapour rises by its own pressure through the jet, and the gas flame raises an inverted mantle to incandescence.

Acetylene lighting depends on burning the gas from a steatite burner, usually giving two fine jets of flame impinging upon one another. The acetylene may be generated *in situ* from carbide, or it may be obtained from cylinders containing the gas in solution in acetone. Under ten atmospheres' pressure acetone dissolves 200 times its own volume of the gas. A mixture of petrol and air can be used in conjunction with a gas-mantle.

A useful gas which is gradually going out of use exists in Pintsch gas. Made from petroleum oil, this gas does not deteriorate under compression to anything like the same extent as coal gas. This property makes it very suitable for such purposes as railway-carriage lighting, in which small bulk is an advantage. Owing to the danger of fire in cases of accident the use of gas for trains is rapidly becoming obsolete. Lighting by means of town gas remains a considerable industry in spite of the steady advance of electrical illumination. The incandescent mantle, as is well known, consists of a fibre framework soaked in a solution containing salts of thorium and cerium ($Ce(NO_3)_2$ 1 per cent., $Th(NO_3)_4$ 99 per cent.). The fibre is then dried, burnt off and dipped in collodion to give it strength for transport. In recent years " soft " mantles have been made by the use of artificial silk. The burning off and collodionising processes can thus be eliminated. The soft mantle is said to maintain its efficiency longer than the hard mantle. It is interesting to compare the " upright " and " inverted " mantles from the point of view of performance. The inverted mantle is by general consent the more able to withstand shock, it distributes the light more conveniently than the upright mantle, and the combustion of the gas is less incomplete with the inverted type owing to the preliminary heating which occurs.

Walsh, in his *Elementary Principles of Lighting and Photometry*, states that a modern mantle of the best quality should give 12 candle-power per cubic foot of gas (500 B.Th.U.) per hour, and that the deterioration should not exceed 10–20 per cent. in the first 1,000 hours.

With special devices the candle-power on low-pressure gas can be increased to 15. The efficiency of gas lighting is seriously impaired if the pressure falls below two inches of water; it may be very considerably reduced by faulty air regulation; and it depends to some extent on the quality of the gas. The factor last mentioned is of interest to the chemist for several reasons. Too rich a gas causes incomplete combustion and consequent sooting of the mantles, unless the air inlet is properly adjusted. This, however, is largely a matter for the consumer. The quality of the gas should not be allowed to fluctuate outside a fairly narrow range. The importance of quality has now been recognised by legislation. The Gas Regulation Act (1920) requires those gas undertakings which have voluntarily come within its scope to appoint independent gas examiners to test the gas periodically in respect of pressure, calorific value, and freedom from sulphuretted hydrogen. The Local Authority or Gas Company undertakes to provide gas of an average calorific value of, let us say, 470 B.Th.U. per cubic foot, free from sulphuretted hydrogen and at a pressure of not less than a specified number of inches of water (usually two) above atmospheric pressure. Quarterly reports, which must be accessible to the public, are issued which indicate the extent of departures from the declared standards. The testing is under the supervision of the Gas Referees, who are immediately responsible to the State.

The General Notification of the Gas Referees and the Gas Regulation Act (1920), published by H.M. Stationary Office, give full description of the working of the Act and of the official manner of carrying out testings. Alternative forms of apparatus approved by the Gas Referees are described.

The Electric Lamp.—The earliest commercial electric lamp consisted of an evacuated bulb in which a very thin filament of carbon was heated by the current. The incandescent filament rarely if ever attained 2,000°, and the light was intermediate in whiteness between that of a gas-mantle and an oil lamp. A great improvement was effected

by the replacement of carbon by metals such as tantalum and tungsten, which could safely be raised to a much higher temperature. The tungsten lamp gives off a whiter light than most illuminants, it lasts 800–1,000 burning hours, and gives about 0·65 candle (average candle-power) per watt.

Most lamps exhibit a 3·5–4 per cent. increase in candle-power for every 10 per cent. increase in applied voltage. Since the current only increases at about half the rate the voltage increases, an increase in voltage means twice as great a percentage increase in candle-power per watt. Even a 1 per cent. increase in voltage may, however, result in a shortening of the life of the lamp by 15 per cent. Hence it will be seen at once that life testing of lamps is of great importance. (See Walsh, *Lighting and Photometry.*)

The temperature to which a tungsten filament can be raised without appreciable volatilisation can be considerably increased if the bulb is filled with an inert gas such as argon or nitrogen at about atmospheric pressure. The gas-filled lamp has an output of about 1·2–1·3 candles per watt.

On account of its intensity the unshaded bright filament should not, however, be in the direct field of view in a room. For projection work and experiments requiring a point source of light showing a continuous spectrum in the visible the pointolite lamp is of great value. In this lamp a solid lump of tungsten metal acts as the positive electrode. It becomes incandescent as a result of bombardment by a stream of electrons from a negative tungsten plate, while a short tungsten filament covered with refractory oxides acts as the starter for the lamp. The first effect is the emission of electrons from this filament, which then ionise the space between the plate and the positive electrode.

Once the lamp is started the auxiliary short filament is switched out of the circuit.

The Moore Tube.—Modified Geissler tubes operating at high voltages with a local transformer have been found useful, particularly for advertising, since tubes up to 200 feet long may be used. When the lamp is filled with nitrogen the glow is slightly pink, with carbon dioxide the light

resembles daylight very closely, whilst neon gives an efficient lamp with an arresting deep red light. The gases are, of course, at a low pressure.

TABLES (from *The Elementary Principles of Lighting and Photometry*, by J. W. T. Walsh. Reproduced by permission of the Author and the publishers, Messrs. Methuen and Co., Ltd.).

Nature of source.	Approx. brightness. (Candle-power per sq. mm.).
Candle flame	0·005
Paraffin flame	0·01
Acetylene flame	0·04 to 0·08
Incandescent mantle (low-pressure)	0·02 to 0·05
,, ,, (high-pressure)	0·01 to 0·5
Carbon filament	0·6 to 0·8
Tungsten filament (vacuum)	1·5
,, ,, (gas-filled)	7 (average)
Tungsten arc	20
Electric arc	170
Special high-intensity arc	500
Mercury-vapour lamp	0·02
Mercury-vapour lamp (quartz)	1
Moore tube	0·004–0·006
Sun (apparent)	1,200
Moon (apparent)	0·004

Surface.	Reflection ratio per cent.
Pure magnesium carbonate	98
White blotting-paper	82
Silvered-glass mirror	80
White enamel	75
Light grey paint	50–70
Medium grey paint	30–50
Dark grey paint	15–30
Light buff paint	50–60
Sage green paint	40–50
Sky blue paint	30–40
Scarlet paint	30
Brown paint	20
Deal wood	40
Polished nickel-plate	64

Pure $MgCO_3$ is almost a perfect diffusing surface.

Other Light Sources.—All lamps depending on the principle of burning liquids in oxygen (including the Wulf carbon disulphide lamp,[1] which gives light fairly rich in ultra-violet) find very little application. For certain purposes the high-tension disruptive spark discharge between metal electrodes still finds application, although the intensity of the light is feeble. The metals used include aluminium, cadmium, copper, cobalt, iron, nickel, magnesium, tin, lead, tungsten, and zinc.

A suitable circuit for generating the spark is shown on Fig. 5.

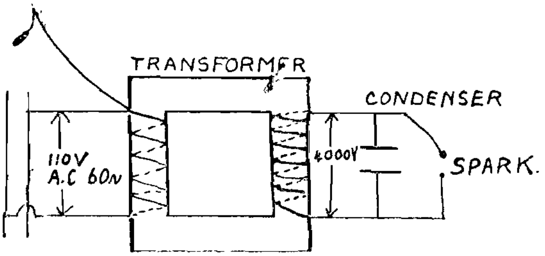


Fig. 5.

The aluminium spark running under water forms a very useful, if feeble, source of continuous ultra-violet radiation. A very fine source of continuous radiation is available in the under-water spark between tungsten electrodes.[2] The author is indebted to Dr. W. R. Brode for the diagram (Fig. 6) of this circuit, which he has set up in the

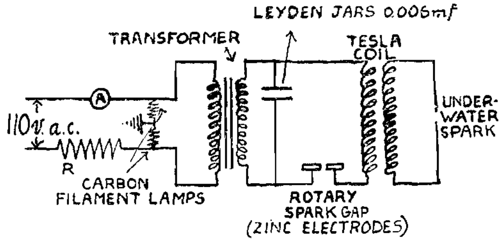


Fig. 6.

Spectroscopy Laboratories in the University of Liverpool. The circuit gives incomparably the finest continuous spectrum with which the writer is acquainted.

A successful source of ultra-violet light exhibiting a continuous spectrum is described by Fulweiler and Barnes.[3] Tungsten rods 3·5 mm. in diameter were mounted in brass rods which screwed into solid rubber stoppers. These were fitted into a pyrex bulb of about 500 c.c. capacity. The electrical circuit requires a step-up transformer of the X-ray type, two condensers of about 0·001 m.fd., and an auxiliary spark gap in series with the tungsten spark. The

latter is about 2 cm. under water, and the former runs most smoothly with an air blast between the electrodes. It is advisable to eliminate self-inductance as far as possible.

The open arc between carbon or metal electrodes forms a specially useful light source of fairly constant high intensity. It is only necessary to connect up a pair of electrodes (which may be of the same or different metals) to a supply of direct-current (lighting circuit) and run the arc at, say, 100 volts 5 amperes (with a variable resistance in circuit) to obtain good results. Much more intense lights can be obtained with higher current consumption. Using iron or iron and nickel electrodes the spectrum extends in air from 2,100–8,500 Å., and consists of fine closely packed lines. Arcs between metallic poles cannot be run successfully on alternating current. Using carbon electrodes the spectrum is continuous and extends into the ultra-violet as far as $280\mu\mu$. When the positive carbon is cored, *i.e.* has a centre of iron, and is used in conjunction with a negative electrode of solid carbon the spectrum extends much further into the ultra-violet. When carbon electrodes are soaked in aqueous solutions of various salts—mineralisers—(such as potassium silicate, potassium carbonate, fluorides, and salts which on gentle ignition leave oxides, rare earth salts, magnesium, and zinc salts) the light approaches in character to sunlight.

A special prepared carbon which is used in actinotherapy is described as having in its centre a complex mixture of rare earth oxides and fluorides obtained as a by-product in the gas-mantle industry. The mixture contains cerium, lanthanum, neodymium, and praseodymium.

Mott and Bedford [4] and Moore [5] found that the flaming white carbon arc greatly excelled all other light sources tried for the photochlorination of methane.

The flame arc is a high amperage arc between specially treated electrodes. Macbeth used 2–4 arcs in series consuming 25 amps. each at 220 volts.

Flame carbons treated with :

(i) Calcium fluoride give a yellow light deficient in blue.

(ii) Strontium fluoride, a red light.
(iii) Copper salt, blue light.
(iv) Silicon or iron salts, reddish-violet.
(v) Lanthanum oxide, pure white.
(vi) Titanium salts, blue.
(vii) Didymium oxide, pure violet.
(viii) Thorium oxide, reddish.
(ix) Ceric oxide, pure blue.

The light of the snow-white flame arc is claimed to be the nearest approach to sunlight plus blue sky of any known illuminant. This applies to both the visible or ultra-violet spectrum.

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Mercury Vapour Lamps.—The first successful mercury vapour lamp was devised in 1901 by Cooper Hewitt. The early experimental lamps failed to run for any length of time, owing to an increase in the electrical resistance as the pressure of mercury vapour grew greater. For satisfactory running the mercury vapour needs to be condensed at the same rate as fresh mercury is vaporised. This rather delicate state of affairs was attained after experiments on the vapour resistance had given guidance as to the suitable dimensions for a tube containing a reasonable amount of mercury.

The next advance was due to Arons, who showed in the following year that a mercury arc could be obtained by passing direct current through an evacuated tube containing mercury vapour. As an illuminant the glass mercury vapour lamp suffers from the disadvantage of giving a very green light, whilst as a source of ultra-violet radiation its value is clearly limited by the poor transmission

of glass. The introduction of clear fused quartz, however, instantly placed the quartz mercury vapour lamp in the forefront as a source of intense ultra-violet light.

The buyer of quartz-mercury vapour lamps now enjoys a very wide choice.

One of the most successful types of lamp is the atmospheric burner, and a convenient one to describe is made by Messrs. Kelvin Bottomley and Baird (K.B.B. Lamp).

This lamp consists of a tube of fused quartz incompletely filled with pure air-free mercury. The negative wire of a direct-current supply is connected to a sealed-in tungsten

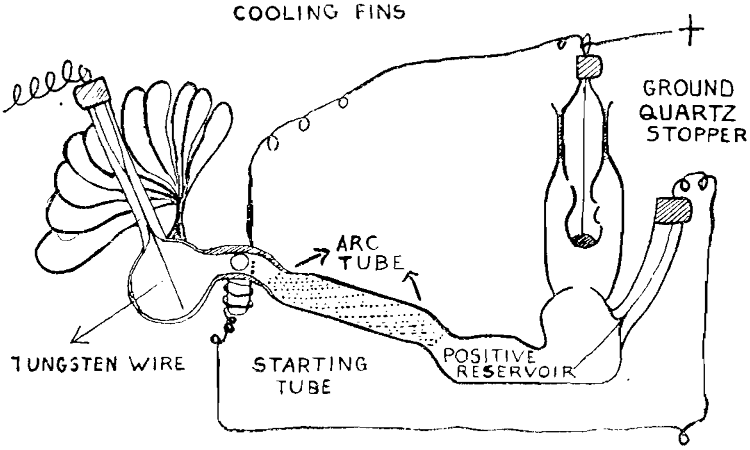

FIG. 7.

wire, which enters a small spherical bulb and dips into liquid mercury. To the negative reservoir are attached two sets of aluminium cooling fins. At the side of the bulb is attached a short curved length of thickened quartz, to which is fastened a short closed side tube called the starting tube. Round this is wound a detachable heating coil. The curved length of quartz opens out into a straight piece of fairly thin quartz known as the arc tube. This is bent downwards and constricted before opening out into a broad capacious section called the positive reservoir. After a constriction at the bend this portion of the lamp

expands into the vertical part, to which the stopper is attached by a ground joint. The positive reservoir is fitted with a diaphragm perforated with a small hole. Inside the positive reservoir the ground-in stopper carries a small bulb with a hole at the side. Inside the bulb is a small globule of mercury into which the positive tungsten wire dips. A third tungsten wire is sealed into the lower part of the positive reservoir by means of a closed side arm. The entire lamp is suspended horizontally.

When the current is applied the level of mercury is at first above the diaphragm but below the little bulb attached to the stopper. The only way for the current to flow through the lamp is via the heating coil to the tungsten wire in the side arm, into the positive reservoir, and through the tube to the negative electrode. After about a minute the mercury in the side arm boils and the mercury vapour causes the appearance of a gap in the continuous column of mercury. The arc is now struck by the current passing through the mercury vapour. As the lamp grows hotter the pressure of mercury vapour increases and drives the liquid mercury back to the constriction and the displaced liquid makes contact with the tungsten wire attached to the stopper. A short-circuit is thus established, which cuts out the heating coil. The lamp will now run steadily, and the mercury vapour in contact with liquid mercury is condensed as fast as formed. The negative electrode is liable to become hotter, but this is compensated by the presence of the aluminium cooling fins. As soon as the current is switched off the stopper bulb becomes isolated as in the beginning.

The idea of the little globule of mercury in the open bulb of the stopper is to ensure that contact is not made directly with the tungsten wire. If when the lamp is running the mercury in the positive reservoir is displaced beyond the constriction, the amperage is excessive. As a rule the arc should not extend beyond the constriction, although it is a common experience that the lamps have a considerable safety factor.

After a few hundred hours' running the lamps deteriorate

rather badly. The stopper can be removed and the mercury carefully emptied out. The entire lamp is then subjected to rigorous chemical cleaning, and then dried. It is advisable to heat the arc tube to redness with a hand blow-pipe if the quartz has become discoloured. This discoloration may then disappear and the quartz may recover its transparency. The output of few lamps is satisfactory after 1,000 hours' running. Some makers claim to be able to recondition old lamps. Various attachments (stands, applicators, etc.) are sold for antinotherapy.

The Vacuum Mercury Vapour Lamp.—This form of lamp consists essentially of a bent U-tube with limbs nearly touching. When the lamp is running the part of the U-tube nearest the bend is horizontal and contains mercury vapour. The arms of the U-tube are bent downwards and the liquid mercury in one forms the negative electrode, whilst that in the other forms the positive electrode.

In the middle of the negative limb there is a sealed-in narrow tube acting as a constriction, and in the corresponding part of the positive limb the arm is flattened a little. Tubes or fragments of quartz or glass are placed between the restricted portions and the terminals. The entire tube is evacuated. The lamp runs on direct current and the current consumption is regulated by a resistance in accordance with the instructions issued by the maker. In order to start the lamp it is fixed in a suitable stand and the operator, wearing dark goggles, tilts it backwards and forwards until the arc is struck. After a little practice a stable arc can easily be obtained.

The deterioration which generally occurs is possibly connected with a mysterious property of fused quartz.* When exposed to intense ultra-violet light for long periods this material, either in the lamp or in test-tube form, develops a purplish colour and its transmission decreases considerably. This appears to be due to a change in the quartz associated with the intake of energy, since when a test tube discoloured in this way is heated to redness in a blow-pipe a sudden

* See Baly and others, *Proc. Roy. Soc.*, 1927. **116A**, 197 *et seq.*

phosphorescent emission occurs, the discoloration vanishes, and the quartz recovers its transparency to ultra-violet rays. This method of reconditioning cannot well be applied to vacuum mercury vapour lamps. It will be noticed that at the inner side of the bend the quartz U-tube is very considerably thickened. The luminous arc takes the shortest

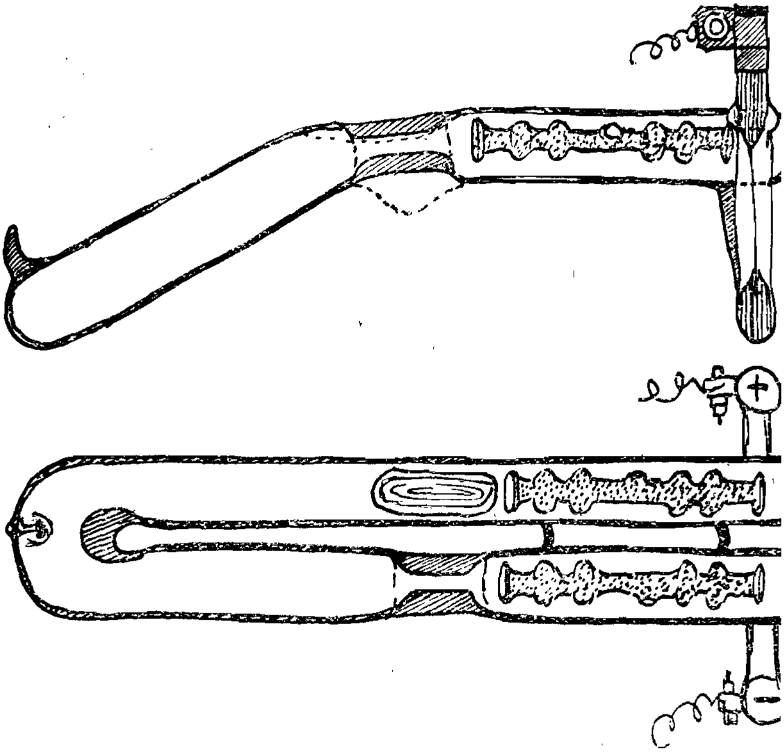

Fig. 8.

path from mercury surface to mercury surface, and this means a high concentration of hot mercury vapour at the inner side of the bend. Any deterioration due to development of pinholes in the quartz will thus occur preferentially at this place, and in order to counterbalance this tendency the quartz is thickened. Experience has shown that lamps not constructed in this way are liable to fail

owing to the appearance of pores and consequent air leaks at the bend.

Mackenzie and King (*Practical Ultra-Violet Light Therapy*) have described an atmospheric lamp cooled by forced draught. They point out that all mercury vapour lamps have a lower working cost than have tungsten or carbon lamps producing the same intensity of radiation. They claim that the atmospheric lamp is superior to the vacuum mercury lamp in this respect. "The atmospheric lamp can be cleaned at intervals from the internal film, whereas the vacuum mercury lamp must be re-made, a far more expensive operation." A longer effective life is claimed for the atmospheric lamp than for the vacuum lamp.

Another successful type of lamp is made by the Hanovia Company. The electrodes are both of mercury and the contacts are made by means of ground joints (employing the metal nickel or the alloy "invar," which possesses nearly the same coefficient of expansion as quartz). There is little that is novel about the lamp from the chemical point of view, but its construction is such that it may be burned at voltages between 90 and 120 on an ordinary 220 volt d.c. supply by using a variable resistance. specially constructed type is available for a.c. supply.

A compact water-cooled quartz-mercury lamp for d or a.c. supply is available in the Kromayer lamp, whi is favoured by practitioners of actinotherapy on accou of the rich emission in the short-wave ultra-violet.

A somewhat different type of lamp is made in whi the anode is made of a metal other than mercury, usua tungsten. The connections are generally sealed-in, a "stitched" or graded glass-to-quartz seals are used order to prevent fracture by differences in expansion. T "Uviarc" lamp is of this type. A spiral of tungsten w is sealed in by a graded glass-to-quartz joint and forms t anode. A metal cap protects the end of the tube and a serves to make contact. The cathode consists of mercu in a specially shaped bulb of thickened quartz. The lar works horizontally or vertically.

Metal Vapour Lamps of Other Types.—Stark and Kuch [1] carried out experiments on metal vapour lamps using cadmium, zinc, lead, bismuth, and antimony. Unfortunately all the lamps proved rather difficult to start, although antimony and cadmium vapour lamps were much easier to start than the zinc and the lead lamps. Lowry [2] introduced the use of the mercury arc for making polarimetric readings, and in order to extend the number of strong lines available an open cadmium-silver arc was devised which worked quite successfully. Later, Lowry and Abram [2] described an enclosed cadmium arc lamp designed to supply the cadmium lines only. The arc is run between water-cooled electrodes of solid cadmium, and as considerable quantities of gas are set free the lamp must be left permanently connected to an air-pump. With a good vacuum it will occasionally start when the current is switched on, but usually an electric spark is necessary.

The most serious difficulty in the manufacture of metal vapour lamps is the danger of the fused quartz cracking whenever the lamp is started or turned off. The cause of failure is, of course, unequal expansion and contraction, and little progress could be made without a solution of the problem of satisfactory metal to quartz seals for the leading-in wires. Sand [3, 4] observed that lead which has been allowed to solidify in contact with glass will if free from oxide form a vacuum-tight joint with the latter. Owing to the very great firmness with which the metal adheres, and owing to its great plasticity, these joints can stand temperature changes without damage. When applied to quartz, the joints are usually made inside a tube in conjunction with a tungsten or molybdenum wire seal, and have proved very successful.

Sand [5] applied this idea to the construction of a cadmium vapour lamp running at a high temperature, the metal being melted by means of a Bunsen burner before starting, so that the arc could be struck by tilting. Once it is started the lamp rapidly becomes hot enough to keep the metal molten. "The principal difficulties to be overcome con-

sisted in the removal of dissolved gases and oxide from the metal and in preventing it from adhering to the glass, so as to avoid fracture of the lamp on heating and cooling. As the lamp is constructed of quartz glass there was also the difficulty of obtaining an efficient vacuum-tight seal for the leading-in wires, but this difficulty was overcome in a perfectly satisfactory manner by the lead-seals described."

The oxide and dissolved gases are removed by subjecting the metal to a process of filtration in a vacuum during introduction into the lamp. The adherence to the glass, which would be very great in the case of a metal freed from its coating of solid oxide, is overcome by introducing into the lamp a small amount of a fine powder which spreads itself out over the surface of the metal. The powder chosen for this purpose was always zirconia, obtained by igniting zirconium nitrate.

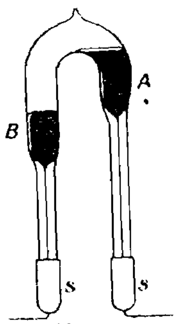

FIG. 9.
(*Physical Society.*)

Fig. 9 shows the general appearance of the lamp. It will be seen that it consists of a quartz tube bent into an inverted U in such a manner as to give rise to a short cathode chamber A and a long anode chamber B. Each of these chambers is continued in a leg consisting of a thick-walled capillary through which a tungsten wire passes, the lead seals *s*, *s* being fitted at the ends of the legs. Figs. 10 and 10*a* illustrate the method adopted to fill the lamp. A small amount of ignited zirconia having been introduced at *a* the lamp is attached to the pump, the piece of cadmium M having previously been placed in a side tube connected with the pump by a tube constricted to capillaries at *b*, *b*, *b* for the purpose of filtering the metal. An alternative plan is shown in Fig. 10*a*, in which the capillaries are dispensed with and the metal is placed in a cage made of iron wire gauze, by means of which the oxide is filtered off. The quartz glass exit tube to the pump is usually connected to the latter by a ground glass joint disposed at right angles to

the plane of the paper, thus allowing the whole lamp to be tilted while evacuated at the pump. After the lamp has been carefully exhausted the metal is melted and allowed to run in.

During this process it is freed not only from oxide but also very largely from dissolved gases. If desired, the metal may be further boiled while the lamp is still at the pump. The lamp when drawn off is now ready for use. A convenient plan for setting it up consists in holding one leg in a clamp and tapping the insulated leading-in wires and terminals on the shank of the clamp so that they may not be twisted off on tilting. This tilting is effected by rotating the shank of the clamp in its boss head. As already mentioned, the lamp is started by heating with a Bunsen burner from the top until the metal is well molten. When started from the cold it usually lights up even before tilting. It was usually run on a lighting circuit of 100 or 200 volts, with a back resistance adjusted to take a current of 5–7 amperes on short-circuit. The voltage on the terminals of the lamp is low, usually about 30. Owing to the fact that the small upper chamber holds the cathode, metal distils into it from the hotter lower anode chamber, and drips back again once every two or three minutes, causing a flicker, which does not, however, interfere with the use of the lamp. It is advisable after use to remove the metal from the

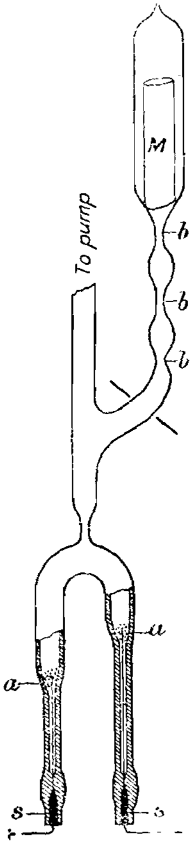

FIG. 10.

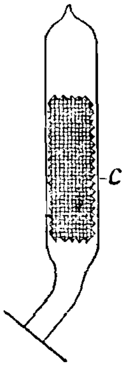

FIG. 10*a*.

bend of the tube, as it would probably otherwise set up strains on solidification which might lead to fracture of the glass."

Lamps were for some time made according to Sand's design by the Silica Syndicate, and used successfully for several years by a number of well-known workers. Difficulties in the manufacture later arose, the cadmium adhering to the quartz, and thus causing the fracture of the lamps. As a result the manufacture of the lamps was abandoned. It is now believed that the difficultly was due largely to the temporary substitution of molybdenum for tungsten leading-in wires in the containers, owing to the better mechanical properties of the former. The molybdenum, however, appears to dissolve in the cadmium, thus lowering its surface tension, with the result that the risk of adhesion is greatly increased.

Bates [6] attempted to construct cadmium vapour lamps after Sand's pattern, and experienced serious adhesion of cadmium to quartz, leading to fracture. He recommends the addition of a small amount of gallium to the cadmium, the alloy, according to his statement, being so soft that no fracture is brought about. It is stated that the containers used by Bates had tungsten leading-in wires, but if, as seems probable, the latter were obtained from the Silica Syndicate, this statement would be incorrect.*

There seems no doubt that satisfactory cadmium lamps can now be constructed.

1. Stark and Kuch, *Physikal Z.*, 1905, **6**, 438.
2. Lowry and Abram, *Trans. Faraday Soc.*, 1911, **7**, 267; 1914, **10**, 103.
3. Sand, *Proc. Phys. Soc.*, 1914, **27**, 127.
4. Sand, *Proc. Phys. Soc.*, 1916, **28**, 94.
5. Sand, E.P. 24766–14; 23854–13.
6. Bates, *Phil Mag.*, 1920, vi, **39**, 353.

NOTES ON TRANSPARENCY OF MATERIALS

The transparency of glasses and other materials can only be determined in a trustworthy manner by quantitative spectrophotometry. As an example of the importance of

* The author is much indebted to Dr. Sand for information concerning his work on the cadmium lamp.

this statement the following instance may be cited from Luckiesh. Most ordinary glasses possess a slight green tinge due to the presence of iron. The spectral transmission of such a glass is approximately complementary to that of a glass containing a little manganese.

Neutralising the green tinge is commonly carried out by adding a little manganese to the melt, but this result is obtained at the expense of a reduction in the transmission of the glass. If iron reduces the transmission by say 5 per cent. and the presence of a little manganese causes a loss of 6 per cent. in transmission, the new glass will have a reduction in transmission of about 11 per cent. As Luckiesh points out, this is a heavy price to pay for the elimination of a slight green tinge.

In this connection Luckiesh's[1] observations on the purple colour of lamp globes are of interest. This is frequently brought about as a result of the exposure to light or X-rays of glasses containing manganese. The colour is not stable, as it disappears under the moderate heat of a Bunsen burner long before the glass loses its rigidity.

The discoloration of glass as a result of exposure to radiation is not confined to manganese glasses. Potash glasses free from manganese develop a bluish colour, whilst sodium glasses may become yellowish-green.

In view of the magnitude of the loss in transmission which occurs in some glasses exposed to solar or intense ultra-violet radiation, it would seem wise to tolerate the slightly greenish tinge of ordinary glass until a better means of neutralising the colour is obtained. For outdoor illumination the use of manganese in glass would seem disadvantageous. Another interesting observation by Luckiesh is that the addition of a very small amount of cobalt to a lead-soda glass increases the ultra-violet transmission to a small but definite extent.

The foregoing paragraphs indicate very clearly that mere visual inspection of glass is useless, and accurate spectroscopic data must be available.

Coloured Glasses.—For most coloured glasses the

subjective colour is the principal criterion. Spectroscopic control serves a useful purpose in controlling manipulations analogous to the combination of pigments. The results are, of course, not always additive, because chemical effects may occur.

The safest protective glasses are so dark (either red or green) that it is impossible to see anything clearly when wearing them in daylight. With quartz mercury vapour lamps or arcs the light is, however, intense enough for comfortable working.

Many makers now advertise glasses to which spectrophotometric guarantees are attached. Any glass which transmits beyond $350\mu\mu$ at 1 mm. thickness should be rejected. For work with relatively feeble lights containing much ultra-violet radiation thick orange glasses are recommended.

Crookes glasses are soda-lime glasses containing cerium nitrate and other ingredients, and are brilliantly clear yellow in colour, but their transmission ceases at $365\mu\mu$ or thereabouts (see next page).

Zsigmondy[2] has given exact information on the colour of glasses of definite composition. On account of the poor transmission of ultra-violet light by glass open arcs and sparks were until recent years the only useful sources of artificial ultra-violet radiation of high intensity. The recent advances of photochemistry and actinotherapy depend to a large extent on transparent fused silica, which made the modern mercury vapour lamp possible.

TRANSPARENCY OF MATERIALS.

Substance.	Limit of transparency.
Flint glass, 2 mm.	$275\mu\mu$
,, ,, 1 mm.	$315\mu\mu$
Crown glass	$295\mu\mu$
Mica, 0·5 mm.	$280\ \mu\mu$
*Uviol glass, 1·3 mm.	$253\mu\mu$
*Vita glass, 1·3 mm.	$275\ \mu\mu$
†" Pollapas " (certain specimens)	$250\mu\mu$
Pure water	$200\mu\mu$
Quartz, 5–10 cm.	$180\mu\mu$
Fluorspar, 1 mm.	$120–130\mu\mu$
Window glass, 2 mm.	$320\mu\mu$
Celluloid film	$300\mu\mu$

* Proprietary glasses. † A new transparent organic product.

TRANSPARENCY OF MATERIALS—*continued.*

Substance.	Limit of transparency.
Crookes glass *	$365\mu\mu$
,, ,, †	96 per cent. infra-red absorbed.
,, ,, for lenses ‡	Nearly all visible transmitted pale blue, $365\mu\mu$
(See *Phil. Trans.*, 1914, A. **214**, 1.)	
Quartz with silver film	Transparent to u.v. only.
Chance's ultra-violet glass	Almost opaque to visible, transmits $390\mu\mu$–$330\mu\mu$

COLOURING MATERIALS FOR GLASS (SODA-LIME).

Colour.	Material used.
Red	Copper, gold, selenium (goes brown in light).
Blue	Cobalt.
(NOTE.—Cobalt glass transmits a deep red band.)	
Pink	Gold in low concentrations, manganese.
Yellow	Carbon, sulphur, uranium, silver, nickel, selenium.
Grey	Nickel, manganese, iron, cobalt.
Green	Iron, copper.
Olive-green ..	Iron, chromium.
Purple	Nickel.
Blue-green ..	Copper.
Blue-violet ..	Cobalt.

No single element isolates spectral yellow.

When a glass containing a little gold is reheated the red colour is usually very much enhanced.

Excessive exposure to radiation exerts very harmful effects on the eyes. Satisfactory protection can only be ensured by the use of goggles, which eliminate glare by a reduction of light intensity and which prevent the transmission of ultra-violet radiation of wave-lengths shorter than $365\mu\mu$, and very largely eliminate infra-red rays. It is important to protect the eyes from reflected ultra-violet rays. In industrial operations, such as arc welding, the radiation may penetrate clothing and cause blisters and ultra-violet burns which heal slowly. The face, hands, and abdomen should be carefully protected whenever high intensities of ultra-violet radiation are in use.

Clear Fused Quartz.—The quartz-mercury vapour lamp is of such importance to photochemistry, and fused quartz to chemistry in general, that an account of its manufacture will not be out of place.

* Fused glass 83 per cent. ; Cerium nitrate 17 per cent.

† Fused soda-glass, 96·8 per cent. ; Ferrosoferric oxide, 2·85 per cent. Carbon—a little tartrate, 0·35 per cent.

‡ Rare earth oxides.

The thermal properties of fused quartz were discovered in 1839 by Gaudin. Until the present century "fused quartz" meant the more or less opaque material obtained by the fusion of sand. Small lengths of a high-quality material were made by piecing together fragments of rock crystal heated in an oxygen–coal gas blow-pipe flame. Alternatively the length of fused material was increased by adding pure silica powder from time to time until the maximum size had been reached. This was conditioned by the heating power and size of the flame.

Berry, Miller, and Devers[4] of the General Electric Company have developed a method of producing fused quartz by means of the electric furnace. The raw material consists of water-clear natural crystal with less than 0·02 per cent. of impurity other than superficial iron oxide, etc., which is removed by washing in acid.

The quartz crystals are packed as tightly as possible into a graphite or carbon crucible. When quartz crystals are heated between 500° and 600° C. they crack and disintegrate, owing to (*a*) the strain set up as a result of the difference in the coefficient of expansion along the two axes, and (*b*) the presence of inclusions of carbon dioxide and water.

Consequently the tighter the crystals are packed during the initial fusion the less chance there will be of the escaping gas forming bubbles in the fused mass. The crucibles are placed in a vacuum electric furnace, which is very rapidly heated to some 1,800° C., for about 45 minutes. The result of the first fusion is a clear mass with a few bubbles ranging from a pin-point to 3 mm. in diameter. The "slug" is now placed in another graphite crucible, which is suspended in a vertical carbon tube furnace. When the mass is fused a graphite piston which just fits the crucible is pressed down by a weight and effects the collapse of the bubbles. The quartz can now be extruded as tubes or rods.

When large blocks, free from bubbles, are required, the quartz is again fused in a vacuum furnace designed to withstand high pressure. As soon as the material is fused the vacuum pumps are cut off and the pressure in the

tank is brought up to a high value in less than a minute. The pressure collapses the bubbles and a product is obtained which is as free from bubbles as many kinds of the best optical glass. To obtain this result it has been found best to raise the temperature quickly to 1,400°–1,500°, at which point the pieces first begin to coalesce. At about 1,750° C. the quartz is thoroughly fused, but very viscous. At 2,000° the liquid is still very viscous. Vaporisation of fused quartz is rapid at 1,600°, and at 1,750° the loss due to evaporation is very great.

The following applications are of interest—prisms, lamps, projection lenses, thermometers, tuning forks, in each case either the optical transparency or the low thermal expension being utilised.

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2. Zsigmondy, *Ann. Physik.*, 1901, iv, **4**, 60.
3. Crookes, *Phil. Trans.*, 1914, **214A**, 1.
4. Berry, Miller and Devers, *Amer. Electrochem. Soc.*, 1924, *Gen. Elec. Rev.*, June, 1924; B.P. 222,119, Dec. 9, 1924.

PIGMENTS

It is interesting to consider the types of compounds used as pigments. Probably metallic oxides and sulphides account for more than half of the useful compounds. Among the oxides we find chinese white (zinc oxide); burnt umber (oxides of iron and manganese); the ochres (consisting of oxides of iron in various forms); viridian and other green pigments utilising oxides of chromium; the beautiful cobalt blue pigment containing aluminium and cobalt oxides; cobalt green consisting of zinc and cobalt oxides. Red lead, another oxide pigment, has the disadvantage of not being inert.

The sulphides are especially rich in yellows. Cadmium or aurora yellow, antimony yellow, and realgar, arsenic sulphide or King's yellow belong to this class. Vermilion (mercury sulphide) is an attractive colour which suffers from the disadvantage of a tendency to blacken when used in water-colour painting. The carbonates are represented by whitening (calcium carbonate), white lead (basic lead carbonate), malachite (a green natural copper carbonate),

and an emerald green substitute consisting of a mixture of alumina and copper carbonate.

The chromates of barium, strontium, and zinc find some application, and lead chromate as chrome yellow has undoubted advantages. Other salts in use are: tungsten green (chromium tungstate); baryta white (barium sulphate, a good white of rather low covering power); terre verte (a naturally occurring silicate containing iron, manganese, and potassium); Freeman's white (lead sulphate); Naples yellow (lead antimoniate); and permanent violet (consisting of manganese phosphate).

Many valuable pigments consist of basic salts. In addition to white lead we have emerald green, a basic cupric aceto-arsenite; Schweinfurt green, a basic arsenite of copper; and verdigris, a basic copper acetate.

Mixed salts occur in cobalt violet, cobalt arsenate and phosphate, and various intermediate colours. Complex salts find much application. Potassium cobaltinitrite, $K_3Co(NO_2)_6$, is a good orange-yellow pigment, although "cobalt yellow" is usually a di-potassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$, but some doubt exists as to the permanence of this compound. Prussian blue, formed by the precipitation of a ferric salt by means of potassium ferrocyanide, is perhaps the classical instance of a complex compound acting as a pigment. Antwerp blue consists of Prussian blue with the addition of a white diluent.

Ultramarine, one of the most beautiful pigments we possess, is found in nature, and may be closely imitated by a process involving the heating under defined conditions of carbon, sulphur, soda, and china clay in a furnace. Carmine, purple, and crimson lakes are made from the cochineal insect, whilst the yellow lakes are derived from quercitron bark. Indian yellow, gamboge, sap green, and natural indigo are of vegetable origin.

The range of pigments now available has been enormously extended by the advent of coal-tar dyestuffs, but great caution must be observed in the use of synthetic pigments unless their permanence has been thoroughly tested.

The following pigments have been found by experience to be fugitive: Asphaltum, brown pink, carmines, crimson lake, indigo, magenta, mauve, sap green, yellow lake.

The following pigments are suspect: Chrome greens, Italian pink, cinnabar greens, lead chromate—Prussian blue mixtures, Vandyck brown, malachite green.

Messrs. Reeve recommend for oil paintings: Flake white, lemon yellow, mid-cadmium yellow, yellow ochre, raw sienna, venetian red, scarlet vermilion, rose madder, burnt umber, ivory black, cobalt violet, and ultramarine. In addition, Messrs. Nisbet favour aureolin, terre verte, Caledonian brown, and Antwerp blue (although this latter is only fairly permanent).

The following precautions are generally advised. Indiscriminate mixing of inorganic and synthetic organic pigments is likely to impair the permanence of work. Aureolin should not be mixed with madder or alizarin. Flake white (white lead) is obviously dangerous when mixed with cadmium yellow.

Titanium pigments do not "chalk" on weathering, and for many purposes a pigment based on the relatively inactive oxide possesses great attractions (cf. E.P. 243081, Aug. 8, 1924; 252262, Nov. 28, 1924).

An interesting application of pigments has been made by Sheringham (Fig. 11). For painting and the matching of coloured fabrics in artificial light serious difficulties arise from the fact that the spectral distribution of energy is usually different from that found either with direct sunlight or diffuse daylight. Sheringham employed a double-tinted reflector in conjunction with an ordinary metal filament lamp so adjusted that the greater portion of the light emitted would strike the reflector. The surface of the reflector is covered by washes of about equal areas of green and violet pigments. As a result the spectral distribution of the light approaches nearer to that of the north skylight.

Messrs. Chance Bros. now make a tinted glass which may be used as a selective filter for the light from a half-watt

lamp. This material gives a good approximation to daylight for the purposes of colour matching.

The importance of this work may be gauged by the quotation of one or two instances (after Martin and Gamble's "Colour"). A fabric dyed with benzyl-violet 5BN and quinoline-yellow appeared moss-green in colour in blue skylight, whilst in artificial light it appeared quite brown

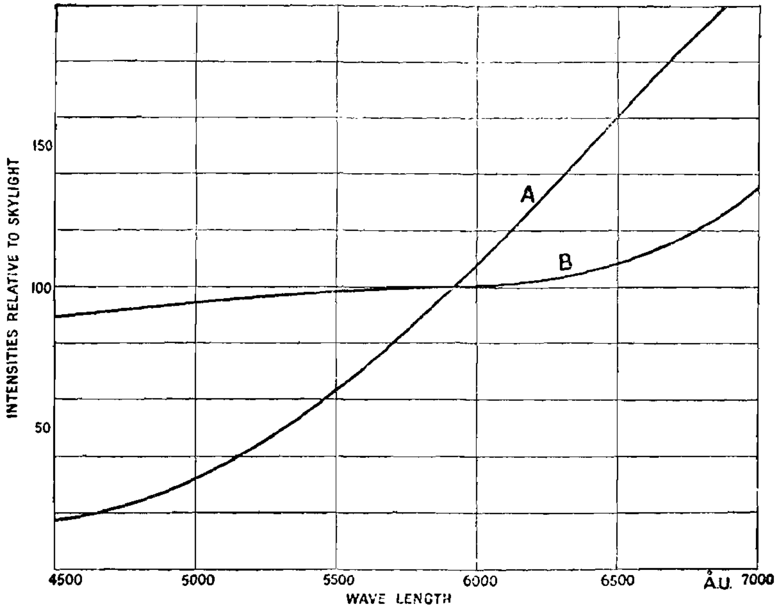

FIG. 11.—Spectral distribution curve for Sheringham daylight lamp. Curve A—gas-filled lamp alone. Curve B—with Sheringham reflector.

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In the second case, benzyl-violet 5BN, formyl violet 10B, and quinoline yellow were the dyestuffs used. In blue skylight the fabric matched with a navy blue, whereas in artificial light it appeared quite a dull red in colour. These examples are no doubt extreme, but they raise in a striking way the whole subject of the specification of the colour of pigments. As long ago as 1892 [2] the necessity for artificial daylight was realised, and both selective absorption and

selective reflection were tried. Dufton and Gardner found a copper glass with a trace of uranium to be effective with the enclosed arc. Dyed gelatine films have also been proposed, but the colours are somewhat fugitive.

An exact description of the optical properties of a pigment is a matter of some difficulty. "Blue" may mean anything from Prussian blue to copper sulphate. Two American reports have been issued aiming at an accurate

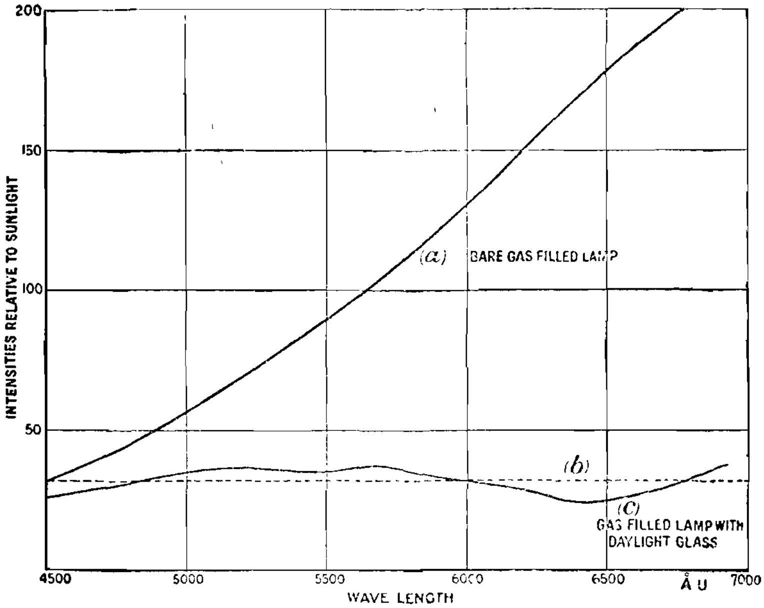
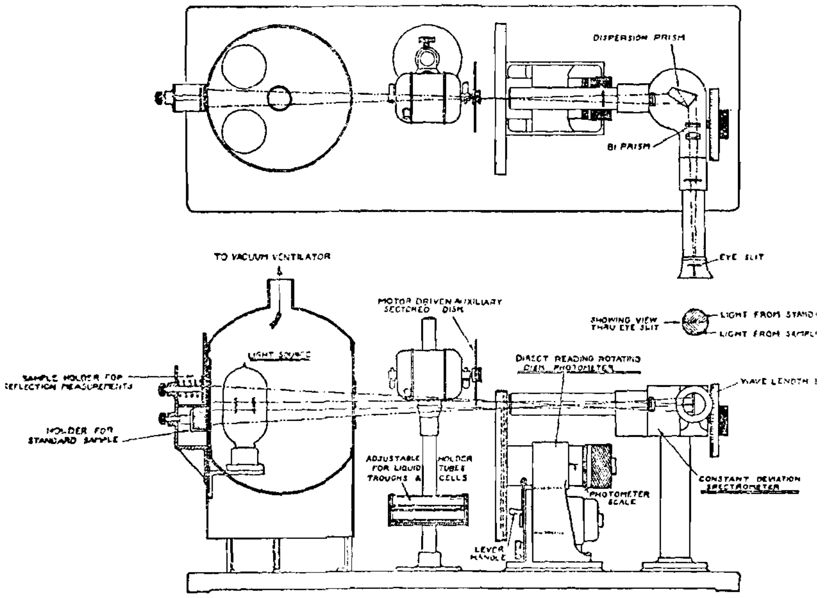


FIG. 12.—Spectral distribution curve of Chance daylight glass (curve supplied by the Research Laboratory of Messrs. Chance Bros. & Co., Ltd.).

Reproduced from "The Elementary Principles of Lighting and Photometry," by J. W. T. Walsh, by permission of the Author and the publishers, Messrs. Methuen and Co., Ltd.

means for the specification of colour. One attacks the problem from the standpoint of colorimetry [3] and the other from the side of spectrophotometry.[4] The Keuffel and Esser direct-reading colour analyser consists of a constant deviation spectroscope fitted with a system of rotating sector disks for obtaining definite reductions in light intensity, two 400-watt projection lamps, and various accessories.



COLOR ANALYZER

FIG. 13.

Reproduced by permission from the Journal of the American Chemical Society.

The above diagram taken from Brode [5] is largely self-explanatory.

It is difficult to illustrate the scientific investigation of the optical properties of pigments in a general comprehensive fashion, and perhaps the best course to adopt is to select an investigation which covers much of the ground and deal with it in some detail. A suitable paper is available in the work of Hill and Howell on " Crystal Structure and Absorption spectra of Cobaltous Compounds." [6]

It is well-known that solutions of cobalt chloride, sulphate, nitrate, etc., are of a rose-pink colour. If, however, concentrated hydrochloric acid or a solution of magnesium chloride is added to cobalt chloride, or even if the latter is dissolved in alcohol, an intensely blue solution results. Interesting as the colour changes of cobalt chloride are in themselves, they acquire an added interest when we remember that cobalt blue and cobalt pink are two well-

known pigments. It was clearly of interest to seek a correlation between the colour changes in solution and the variability of the colour of cobalt oxide-metallic oxide preparations. Accordingly a series of pigments were prepared. Essentially the pigments consist of a homogeneous non-fused mass of oxides, and they may be prepared simply by heating together a mixture of oxides. "It is, however, advantageous to use the sulphates, because on warming they melt in their own water of crystallisation giving a perfect mixture, and on further heating evolve sulphur dioxide, yielding a friable and completely oxidised mass."

The mixed sulphates (or oxides when these are not available, *e.g.* stannic oxide or silica) are therefore heated gently at first and finally at about 1,200° for half an hour. An interesting point then arises that the pigments as thus prepared are too intensely coloured for examination. Accordingly, diluted colours were obtained by the addition of zinc or magnesium oxides.

The following diluted pigments were used :

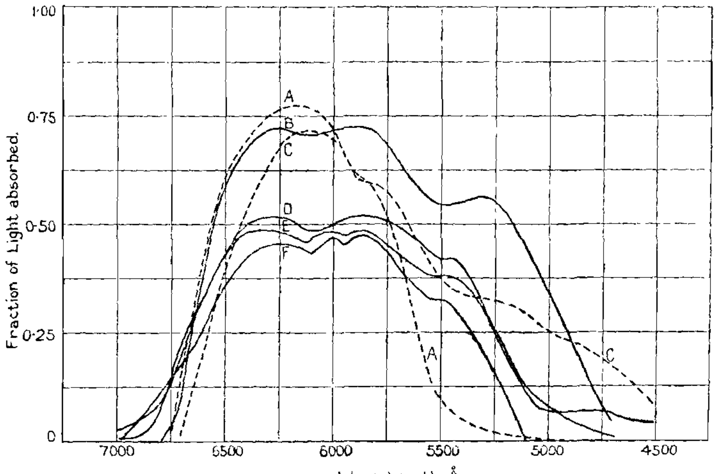
Thenard's blue or Cobalt blue ..	(*a*) $CoO.Al_2O_3$	$32MgO.Al_2O_3$
	(*b*) $CoO.Al_2O_3$	$32BeO.Al_2O_3$
	(*c*) $CoO.Al_2O_3$	$32ZnO.Al_2O_3$
Cerulean blue	(*a*) $CoO.SnO_2$	$32MgO.SnO_2$
	(*b*) $CoO_2.SnO_2$	$32MgO_2.SnO_2$
	(*c*) $CoO_2.SnO_2$	$32ZnO_2.SnO_2$
Cobalt orthosilicate	(*a*) $CoO_2.SiO_2$	$4MgO_2.SiO_2$
	(*b*) $CoO_2.SiO_2$	$32ZnO_2.SiO_2$
Rinmann's green	CoO ; 256Zno	
Cobalt pink	CoO.8MgO	

The pigments were examined spectroscopically in order to determine the spectral distribution of the reflected light. Small boxes were made of cardboard in the form of a cube with two of its adjacent faces missing. The inside of one such box was covered with a thick layer of the pigment, and a similar box was used as a blank. The latter was coated with the gum arabic solution used for distributing the pigment. The boxes were then arranged so that an open side of each faced the apertures of a Nutting photometer ; above the boxes was placed a powerful half-watt lamp, so that the light entered the boxes via the other open side.

The reflected light was then studied in detail, the Nutting photometer fixing the intensities of light of various colours dispersed by means of a Hilger wave-length spectroscope.

Various solutions of cobalt salts were also examined after the apparatus had been suitably adapted.

The crystal structure of spinel ($MgOAl_2O_3$, or $MgAl_2O_4$) has been elucidated by means of X-rays by W. H. Bragg (*Phil. Mag.* (2) xxx. p. 309, 1915), who showed that each magnesium atom is surrounded by four oxygen atoms.



Messrs. Taylor & Francis.] [*Philosophical Magazine.*

A. Cobalt thiocyanate in ether (1/20,000).
B. Cobalt oxide in potassium hydroxide (1/40).
C. Cobalt thiocyanate in potassium thiocyanate (1/40).
D. Cobalt blue (*b*) $CoOAl_2O_3,32BeOAl_2O_3$.
E. Cobalt blue (*a*) $CoOAl_2O_3,32MgOAl_2O_3$.
F. Cobalt spinel.

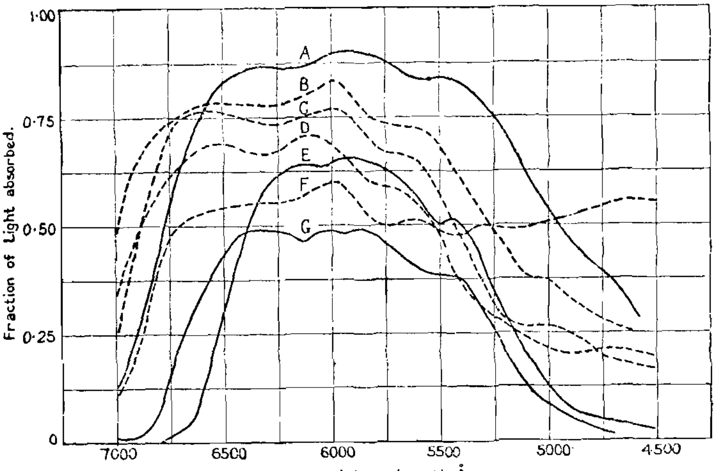
FIG. 14.

The magnesium atoms in spinel may be partly replaced by cobalt giving the blue cobalt spinel.

The curves for cobalt spinel and cobalt blue are almost identical (Fig. 14). It is therefore reasonable to conclude that the structure of cobalt blue is identical with that of cobalt spinel. Since cobalt spinel is a solid solution, it follows that in both cases the cobalt atom replaces the magnesium atom without change in structure, and is therefore surrounded by four oxygen atoms.

The absorption curve for cobalt blue with beryllium as diluent (Fig. 14) is of precisely the same nature as with magnesium as diluent.

Zinc is known to form a spinel with the same structure as magnesium spinel, and it may be replaced by cobalt yielding a blue pigment just as magnesium is so replaceable. The absorption spectrum of this compound (Fig. 15) is strictly comparable with that of cobalt blue with magnesium



Messrs. Taylor & Francis] [*Philosophical Magazine.*

A. Cobalt orthosilicate (*b*) $(CoO)_2SiO_2,32(ZnO)_2SiO_2$.
B. Cerulean blue (*b*) $(CoO)_2SnO_2,32(MgO)_2SnO_2$.
C. Cerulean blue (*a*) $CoOSnO_2,32MgOSnO_2$.
D. Rinmann's green, CoO,256ZnO.
E. Cobalt blue (*c*) $CoOAl_2O_3,32ZnOAl_2O_3$.
F. Cerulean blue (*c*) $(CoO)_2SnO_2,32(ZnO)_2SnO_2$.
G. Cobalt blue (*a*) $CoOAl_2O_3,32MgO,Al_2O_3$.

FIG. 15.

as diluent (reproduced again for comparison in Fig. 15). The absorption bands are exactly similar. The curves show that the effect on the absorption spectrum of introducing zinc for magnesium is extremely slight, thus clearly revealing the CoO_4 group as a distinct entity.

Cerulean blue is stated to be a compound of cobalt oxide and stannic oxide. It has been investigated by Hedvall (*Arkiv. Kem. Min. Geol.* (18), v., p. 1, 1914), who prepared cobalt ortho-stannate Co_2SnO_4 which he found was green,

but that if more stannic oxide was used the product became bluer in proportion to the excess employed.

By introducing an equivalent amount of magnesium for cobalt in the ortho-stannate, a perfectly blue product is obtained which corresponds exactly in colour and intensity with the artist's pigment "cerulean blue." It is seen that this compound (Fig. 15) has precisely the same absorption spectrum as one having double the amount of stannic oxide (Fig. 15). It therefore follows that in both cases the cobalt is present as the ortho-stannate; the function of the excess of stannic oxide must be the same as that of the magnesium oxide.

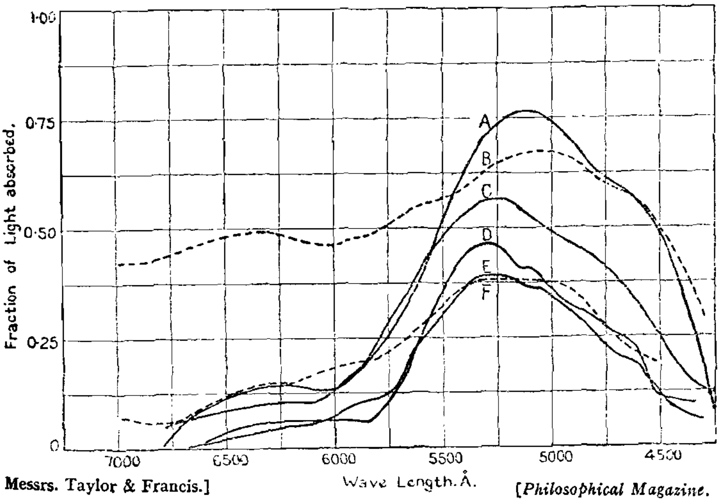
By introducing zinc instead of magnesium a dull green compound is obtained. This would appear to correspond more nearly to the green pure ortho-stannate, since the atomic weight of zinc is approximately the same as that of cobalt. It will be seen, however, that the absorption spectrum of this compound (Fig. 15) is exactly similar to that of the other two stannates with an additional absorption in the violet.

Now the crystal structure of zinc oxide has been elucidated by W. L. Bragg (*Phil. Mag.*, xxxix., p. 647, 1920) by X-ray measurements, and he showed that the zinc atom is surrounded by four oxygen atoms. The cobalt atom replacing the zinc is consequently similarly situated, and there seems no doubt, therefore, that in all these compounds the cobalt atom is surrounded by four other atoms.

Both in the blue solids and blue solutions the cobalt atom is in immediate association with four atoms or groups.

The structure of magnesium oxide has been investigated by Wyckoff (*Amer. Journ. Sci.*, i., p. 138, 1921), who found it was of the same type as that of rock-salt; the magnesium atom is surrounded by six oxygen atoms. Cobalt replaces the magnesium in the oxide, giving a red compound. The cobalt atom is here surrounded by six oxygen atoms, and the absorption spectrum (Fig. 16) is of an entirely different type from that of the blue pigments. It is suggested that just as in the blue compounds the colour is due to the association of the cobalt atom with four groups, so also in the red compounds the colour is due to its association with six.

The cobalt ortho-silicate with magnesium as diluent is red and gives a very similar absorption spectrum (Fig. 16) to that of cobalt oxide in magnesium oxide. With zinc as diluent, however, the compound is blue, and gives an absorption spectrum (Fig. 15) absolutely comparable with that of cobalt blue. It is evident that the two compounds are of entirely different structure. It would appear that in



Messrs. Taylor & Francis.] [*Philosophical Magazine.*

A. Cobalt chloride, sulphate, or nitrate (1/50).
B. Cobalt orthosilicate (*a*) $(CoO)_2SiO_2,4(MgO)_2SiO_2$.
C. Cobalt tartrate in potassium tartrate (1/10).
D. Cobalt oxalate in potassium oxalate (1/10).
E. Cobalt formate in potassium formate (1/10).
F. Cobalt pink CoO,8MgO.

FIG. 16.

the former the cobalt atom replacing the magnesium i associated with six groups. In the latter, the zinc atom which has a strong tendency towards association with fou groups, is so situated, and the cobalt atom replacing it take the same structure, yielding a blue compound.

The following references may be useful to those wh wish to pursue the subject of colour-measurement further:

Theory and Practice in Colour Measuring and Recording.
A. E. Bawtree, *Jour. Oil and Colour Chemists' Assn.*, 1921, **4**, 165.
A Comparative Study of Methods used for the Measurement of Colour.
T. M. Lowry and L. P. McHatton, *ibid.*, 189, and **5**, 351.
The Lovibond Colour System.
Sci. Papers, U.S. Bureau of Standards, No. 547, 1927.

SECTION III.—MEASUREMENT OF LIGHT INTENSITY

The Problem.—In many photochemical processes it would be a great convenience if the directions for carrying out a preparation successfully could include some such phrases as the following: expose at a distance of x inches from a mercury lamp of dimensions y running at a voltage v and an amperage a, or a carbon arc under similarly defined conditions. Unfortunately it is quite impossible to secure reproducible results in this way, because other variables such as the age of the lamp, the physical condition of the quartz, etc., interfere seriously. There are two alternative ways of tackling the difficulty, namely, determination by physical methods of the light energy emitted, and control by means of simple actinometric chemical changes.

It must be admitted at the outset that no chemical method can compete for the most exact work with physical measurements using thermopile-galvanometer systems calibrated against standard sources. Such measurements are outside the scope of this work, and reference should be made to the following papers:

Warburg, *Sitz. preuss. Akad.*, various memoirs, 1911–1919.
Eggert and Noddack, *ibid.*, 1921–1923.
Kornfeld, *Z. Wiss. Phot.*, 1921, **21**, 66.
Gruss, *Z. Elektrochem.*, 1923, **29**, 144.

Any reaction to be used in measuring light intensity should obey the Lambert-Beer-Grotthus-Draper Laws, *i.e.* $dc/dt = kI(I - e^{-ecd})$, k being a constant connecting the reaction rate dc/dt with the absorption.

Perhaps it ought to be explained that the need for controlling the output of light sources by chemical means is

only acute for ultra-violet light, as visible light can usually be specified in terms of candle-power. Moreover, the importance of visible light to laboratory photochemistry is quite small compared with that of ultra-violet light, if we except for the moment the subjects of photography and plant photosynthesis, which both occupy a somewhat peculiar position. A large number of reactions have been suggested as suitable for ultra-violet actinometry, but no single one has proved entirely satisfactory. That the problem is a complicated one may be seen from the following considerations :

(*a*) The well-known Grotthus-Draper Law generalises our experience that only those rays which are absorbed can effect photochemical changes.

(*b*) Every substance has its own absorption spectrum, and every photochemcial change its own spectral distribution of efficiency, which only occasionally bears a simple relation to the absorption of the reactants.

(*c*) The majority of photochemical reactions do no proceed simply enough to provide direct evidence of having reached a definite stage.

(*d*) Every source of ultra-violet light has its own spectra energy distribution.

(*e*) The deterioration of some light sources with time e.g. quartz lamps, is a very uncertain factor.

A single general purpose method would probably be failure for reasons of which an instance may now be given.

Consider a reaction A→B which occurs with light on th short-wave side of 260$\mu\mu$ so that a test suitable for thi change will need to be affected only by the range 200–260$\mu\mu$ Now consider a reaction C→D, influenced only by the regio 310–370$\mu\mu$: a method suitable for the first reaction woul give a high reading with a mercury lamp but a zero readin with tropical sunlight, and would therefore be useless fo the second reaction.

It will be seen that the value of a chemical method wil depend entirely on the reaction to be controlled.

Webster, Hill and Eidinow [1] became interested in chemical methods for the measurement of light intensity, largely from the point of view of obtaining a gauge for dosage in light therapy. They reviewed the methods available to them at the commencement of their work, but found no test entirely suitable for the purpose in hand. Before discussing the result of their search for a new method we may first give a brief account of the older tests.

Keller's Modification of the Behring-Meyer Test.—Acidified potassium iodide plus a trace of thiosulphate is exposed to ultra-violet light in the presence of starch, and the time which elapses before the appearance of the blue colour is noted. The mixture for exposure consists of:

> 25 c.c. of 1 per cent. potassium iodide,
> 25 c.c. of 5·3 per cent. sulphuric acid,
> 1 c.c. of N/400 sodium thiosulphate, and
> a few drops of starch solution.

This test gives results reasonably parallel with the erythema producing power of different light sources. The test solution is, however, not very stable.

Eder's Photometer.—In this method a wedge of gelatine of increasing greyness with a scale printed beneath it is used, and sensitive paper of a standard make is placed in a frame beneath the wedge. On exposure of the wedge the extent to which the scale is printed off on the paper is a measure of the intensity of the shorter visible and ultra-violet regions.

Bordier Actinometer.—Paper soaked in 20 per cent. aqueous potassium ferrocyanide changes colour under the action of light, and the extent of the change is gauged by comparison with a set of standard colours. Webster, Hill and Eidinow state that the results of tests carried out under quartz and glass screens were as follow: "That under quartz colours occurred the quicker, but the reaction is very slow, *e.g.* on exposure to a 25 amp. arc slight coloration was shown in exactly 90 minutes, while an erythema of the skin occurred in 15 minutes' exposure, and the acetone

methylene blue (see p. 54) was bleached 1·0 on our scale by an exposure of an hour."

Furstenhaus' Actinometer depends on the change in electrical resistance which occurs on illumination of selenium (see p. 158).

Victor Henri [2] investigated the following methods for gauging ultra-violet light:

Silver Citrate Test.—Paper treated with a solution of silver citrate darkens on exposure to light.

The photochemical *decompositions* of pure *dry hydrogen chloride* and aqueous solutions of *hydrogen peroxide* were also tried. The *decomposition* of *cane sugar* which occurs under irradiation can be followed by the change in hydrogen ion concentration, determined by a physical method. The interposition of a glass screen between the light and the quartz reaction vessel slows the reaction to one-fifteenth or one-twentieth of its original speed. Henri also found that the glass screen reduced the rate of decomposition of potassium iodide in the presence of sulphuric acid to about 20 per cent. of that occurring in the absence of the screen.

Sterilisation of B. Coli.—100 c.c. of an emulsion of B. coli placed in a porcelain capsule 6 cm. in diameter were exposed at a distance of 20 cm. from a quartz-mercury lamp, with and without a glass screen. The bactericidal action occurs from 1,000 to 2,000 times more quickly without the interposition of the glass screen than with it. On the other hand, it appears that the silver citrate paper darkens almost as quickly under glass as under quartz.

None of the reactions known to Webster, Hill and Eidinow proved quite suitable for their purpose, and the subsequent work of these authors will now be given largely in their own words. "The sun varies enormously with its height in the sky and with clarity of the atmosphere, amount of cloud, and so on. A gauge is required to test the strength of the sun before dosage and to measure the dosage given day by day. Seeking for a gauge based on the biological action we first began by trying the bleaching of various solutions of protein and methylene blue, and

then turned to a solution of acetone-methylene blue as simpler and cleaner and having a suitable absorptive power. A solution of acetone in water is decomposed by ultra-violet light with formation of acetic and formic acids and other substances. We first used the increase in p_H of a watery solution of acetone exposed to a source of ultra-violet light as a measure of the intensity of the light and in the laboratory—this gives satisfactory results although some care is needed. The decomposition of aqueous acetone by light is partly an oxidation process, and it was thought likely that reduction processes were occurring at the same time, and that these might be measured by the reduction of methylene blue. This proved to be the case, the bleaching of the methylene blue being proportionate to the time of exposure. Methylene blue evidently acts as a hydrogen acceptor in the complex reduction processes going on in the mixture."

The test solution is made up as follows:

> 5·8 c.c. of a 0·1 per cent. solution of Poulenc Freres methylene blue are added to 30 c.c. of acetone and made up to 100 c.c. with water. This solution is called the standard.

A tiny quartz tube is filled with the test solution, and is exposed to the light for a definite period at a definite distance in the case of an artificial source: a certain amount of bleaching occurs, which is estimated by means of comparison with a set of colorimetric standards. A convenient outfit for carrying out the test is now on the market at a reasonable price.

The following are some typical tests carried out by Mr. A. E. Gillam and the author:

Distance.	Exposure.	Lamp.	Units on the arbitrary scale.
12 inches	4 hours	Old Hewittic	2·5
12 „	3 „	New Hewittic	5·5
12 „	1 hour	New K.B.B.	5·0
12 „	6 hours	Iron-nickel arc	2·2

The effect of interposing screens of vitaglass and ordinary window-glass was next tried. The table summarises the

results of a careful set of experiments which were duplicated as far as the conditions would allow.

Light source.	Units of bleaching per hour at 12 inches. Bare.	Vitaglass screen.	Glass screen
Old Hewittic quartz-mercury lamp	0·60	—	—
New ditto	1·80	0·2	0·08
K.B.B. atmospheric quartz-mercury lamp	5·10	0·67	0·33

The screening experiments indicate ratios bare : vitaglass : window-glass = 100 : 11 : 4·4. ; 100 : 13 : 6·5

Hence in round figures we have :

88 per cent. of the reaction due to rays between 200–280$\mu\mu$
6 ,, ,, ,, ,, ,, 280–325$\mu\mu$
6 ,, ,, ,, ,, beyond 325$\mu\mu$

Now if, as seems probable, the phototherapeutic effects are due to the region 265–305$\mu\mu$, the screening experiments indicate that not more than some 10 per cent. of the reaction is to be ascribed to rays within the "stimulative" region. Another disadvantage of the test is that it is difficult to judge the degree of bleaching with an accuracy exceeding $\pm 0{\cdot}5$ unit, and relatively lengthy exposures are necessary to secure good results. The test is also rather slow in sunlight, but for recording the ultra-violet light reaching the test vessel during a complete day's sunshine this very slowness is an advantage. It is only rarely that the bleaching will exceed 7 units on the scale in a single English summer day, whereas in the Alps 23 units have been recorded. With mercury vapour lamps, particularly at short distances, the test is fairly rapid, and its simplicity, together with the fact that no skill is necessary, make it a very useful method in spite of its limitations.

Another reaction which has been recommended for medical work is the photo-decomposition of *pure* carbon tetrachloride. Mackenzie and King, who first suggested this test in their *Practical Ultra-Violet Therapy* (Benn, 1926), state that the decomposition occurs with rays shorter than 265$\mu\mu$, a statement which we have confirmed. The justification for the method as applied to light therapy is that

the chemically active rays are those which are most valuable therapeutically, a statement which appears to be due to a misconception. Perhaps the first thing which ought to be emphasised in connection with this test is the absolute necessity for *pure* tetrachloride. Massol and Faucon[3] were the first to discover that all ordinary specimens of so-called pure tetrachloride exhibited the selective absorption characteristic of carbon disulphide, which is almost invariably present as an impurity. Now the test suggested by Mackenzie and King fails entirely if the ordinary material is used, because whilst the pure substance decomposes with liberation of chlorine, which may be detected, the impure compound will *absorb* quite an appreciable amount of the gas.

The only satisfactory pure tetrachloride which we have been able to procure is that made by Messrs. Albright and Wilson of Oldbury, and recommended by Mackenzie and King.

The main reaction which occurs is :

$$2CCl_4 \xrightarrow{\text{light}} C_2Cl_6 + Cl_2$$

As a result of a secondary reaction a trace of some unidentified product is formed. In carrying out the test a small stoppered quartz tube of 6 c.c. capacity and 1 cm. diameter and 8 cm. length, or else a hollow cube of fused quartz, is filled with the tetrachloride and exposed for 3 minutes to the source of light. The liquid is then taken and treated with one drop of a 10 per cent. solution of fresh potassium iodide, and is then well shaken. Iodine is liberated in amount equivalent to the amount of chlorine, and the liquid becomes coloured owing to the free iodine remaining in solution. Alternatively the authors suggest the addition of potassium iodide in excess and subsequent titration by means of N/100 sodium thiosulphate. Gillam, working with the writer, found the colorimetric estimation of the iodine by means of standards to be more successful than the titration. No reaction occurred under screens of glass and vitaglass, even with protracted exposures,

whereas the unscreened mercury vapour lamps gave satisfactory colours.

The facts appear to be that the test is suitable for measuring the bactericidal power of a lamp or for detecting the deterioration in output which occurs with time, but that it is not really a good general test for actinotherapy. Its limitations may be put quite briefly : it would give no reaction for Alpine sunlight, whereas the ideal test for actinotherapy must give a marked effect.

It has been suggested by Gillam and Morton [4] that the reaction :

$$KNO_3 \xrightarrow{\text{light}} KNO_2+O$$

may be adapted to measuring the ultra-violet intensity of light sources.

It is claimed in the first place that the reaction is suitable for determining the bactericidal efficiency. A method suitable for this purpose must fulfil the following requirements :

(*a*) The reaction must not be affected by rays longer than $300\mu\mu$, since the bactericidal effect of light only commences at $297\mu\mu$.

(*b*) The photochemical change should begin about $297\mu\mu$, but shorter wave-lengths should be increasingly effective.

The reaction proposed has in its favour the following points :

(*a*) Absorption of light by nitrates commences near $330\mu\mu$, rises to a maximum near $300\mu\mu$, falls to a minimum near $265\mu\mu$, and rises very rapidly beyond this point to $193\mu\mu$. A very thin layer of a moderately strong solution is sufficient to absorb all light shorter than $300\mu\mu$.

(*b*) Warburg [5] has shown that the quantum efficiencies (molecules transformed per quantum absorbed) are :

at $207\mu\mu$	0·25
$253\mu\mu$	0·17
$282\mu\mu$	0·024

There can be no doubt (cf. Villars [6]) of the approximate

correctness of these results. The amount of decomposition is small for wave-lengths between 280 and $330\mu\mu$, and very much greater for rays on the short-wave side of $260\mu\mu$. Theoretically, therefore, the photolysis of potassium nitrate closely resembles the bactericidal reaction in respect of the spectral distribution of photochemical efficiency.

The next step is to determine the use that can be made of this observation. Is the amount of nitrate formed in a short time capable of accurate measurement? Warburg found that the photolysis in polychromatic light proceeded much more rapidly in alkaline than in neutral or acidic solutions, and Villars fixed the optimum condition at a p_H of 9·4. The decomposition may be followed by Villars' modification (*loc. cit.*) of Warburg's iodimetric method. To about 30 c.c. of the solution, 5 c.c. of N/5 sodium hydroxide are first added; then 5 c.c. of 10 per cent. potassium iodide and starch solution as indicator. A rapid stream of carbon dioxide is then blown through the mixed solution, so that after about 3 minutes the whole of the oxygen is expelled. The solution is then acidified with 5 c.c. of 5M oxygen-free sulphuric acid and titrated with N/100 sodium thiosulphate. The exposures necessary for reasonably large burette readings are unduly long if the nitrate photolysis is to be regarded as an ultra-violet actinometer.

There exists, however, an extremely delicate test for the presence of nitrite in the Griess-Ilosvay colorimetric reaction. It is possible to utilise this test as the basis of an actinometer by using nitrate buffered at $p_H = 9·4$. The buffered solution shows an absorption spectrum differing little from that of neutral potassium nitrate. The experimental procedure is as follows:

Stock Solutions:—(a) N/10 KNO_3 buffered at P_H 9·4—

10·1 grams of potassium nitrate,

250 c.c. of a mixture of potassium chloride and boric acid M/5 with respect to each constituent,

160 c.c. of M/5 NaOH (CO_2 free),

made up to 1,000 c.c. with CO_2-free water.

This solution should be kept in a brown glass bottle.

The buffer solutions required for this mixture should be made up according to the directions given in *The Determination of Hydrogen Ions*, by W. M. Clark.

(*b*) *Nitrite reagent.*—This is made up as follows: 0·5 gram of sulphanilic acid is dissolved in 150 c.c. of dilute acetic acid. To this is added a solution made by boiling 0·1 gram of α-naphthylamine with a little water, making the whole up to 300 c.c. with dilute acetic acid. This reagent should be protected from contact with air and replaced if it develops a noticeable pink colour.

(*c*) *Glacial acetic acid.*—A convenient method of using this and the nitrite reagent is to keep them in small bottles through the corks of which 2 c.c. pipettes are placed.

(*d*) *Standard sodium nitrite solution.*—This is best prepared from pure silver nitrite. Concentrated potassium nitrite solution is treated with silver nitrate and the precipitate of silver nitrite filtered and washed with cold distilled water. It is then dissolved in a little hot water and rapidly cooled. The resulting crystals are filtered by suction, washed with cold water, and dried in a desiccator in the dark over calcium chloride. 1·539 grams of the pure dry silver nitrite are weighed out, dissolved in hot water, and treated with a slight excess of sodium chloride to precipitate the silver. The mixture is cooled and diluted to 1 in 50 for use and gives a standard N/5,000 sodium nitrite.

A clear fused quartz test-tube is placed at a measured distance from the light source. For a quartz-mercury lamp the distance is 12 inches in a direction at right angles to the axis of the lamp. The test-tube contains the solution of nitrate buffered at p_H 9·4. After a definite period of exposure 10 c.c. of the solution are removed by means of a pipette and run into a Nessler cylinder. Then 2 c.c. of the nitrite reagent and 2 c.c. of glacial acetic acid are added

and the solution made up to 40 c.c. with distilled water. At the same time another tube should be taken and the same quantities of the test reagent and acetic acid should be added to distilled water and either 1 or 2 c.c. of N/5,000 sodium nitrite added. This solution is made up to 40 c.c. and the two tubes are left to stand for half an hour. The concentration of nitrite formed in the photolysis is then determined by comparing the depths of the two solutions, which give pink colours of equal intensity.

Matching is more easily accomplished by surrounding the tubes with black paper sheaths.

The extreme delicacy of the colorimetric test makes it essential that blank tests should be carried out periodically, and that distilled water should be used throughout.

RESULTS OF ACTUAL EXPERIMENTS

(1) A 6-inch × $\frac{3}{4}$-inch clear quartz test-tube was exposed to a new quartz-mercury vapour lamp for one hour at 12 inches, 10 c.c. of the solution were treated with 2 c.c. of nitrite reagent and 2 c.c. of glacial acetic acid, and then diluted to 40 c.c. and allowed to stand for 30 minutes. The nitrite produced gave a colour equal in intensity to that developed by 6·4 c.c. of N/5,000 nitrite.

(2) An old mercury vapour lamp was treated in exactly the same way, and the nitrite produced in this case equalled 1·6 c.c. of N/5,000 solution. Thus the output of the two lamps as regards the rays detected by this reaction is in the ratio of 6·4–1·6, or 4–1. (The voltage across the lamps was in each case 125, and the amperage 2·4.)

(3) A nickel-iron arc (105 volts 5–6 amps., 40 volts across the electrodes) examined produced nitrite equal to 5·2 c.c. of N/5,000 $NaNO_2$ in one hour at 6 inches.

At 12 inches for one hour this would equal $\frac{5 \cdot 2}{4} = 1 \cdot 3$ c.c. of nitrite, thus indicating that the

nickel-iron arc is only slightly inferior to the old mercury vapour lamp above.

The results of screening experiments were as follow:

	Without screen.	Vitaglass screen. 0·090 in. = thickness.	Window-glass screen. 0·105 in. = thickness.
Mercury vapour lamp (Hewittic), 120 volts 2 amps.	½ hour, 12 ins. =3 c.c. N/5,000 nitrite	6 hours, 6 ins. =2·75 c.c. N/5,000 nitrite	6 hours, 6 ins. =0·9 c.c. N/5,000 nitrite
Calculated per 2 hours at 12 ins.	12 c.c.	0·23 c.c.	0·075 c.c.
Calculated as per cent. of decomposition with quartz	100	1·9	0·625

	Unscreened.	Vitaglass.	Window-glass.
Sunlight, 12.30 to 5 p.m., bright sun 19/5/27.	1·9 c.c. N/5,000 nitrite	1·75 c.c. N/5,000 nitrite	0·5 c.c. N/5,000 nitrite
As per cent. of effect on unscreened quartz	100	92	26

For mercury vapour lamp, vitaglass : window-glass = 3 : 1 } by this test.
For sunlight, vitaglass : window-glass = 3·5 : 1 }

The limiting ultra-violet wave-lengths transmitted by the screens may be taken as very near

vitaglass .. .. .. 275$\mu\mu$
window-glass .. .. .. 325$\mu\mu$

The table indicates that about 98 per cent. of the nitrite formed as a result of exposure to the unscreened lamp owes its origin to rays on the short-wave side of the vitaglass transmission. This serves to fix the *unscreened* reaction as eminently suitable for measuring bactericidal efficiency. It is also suitable for indicating the deterioration of a lamp, since this phenomenon begins in the short-wave ultra-violet region to which the nitrate photolysis is very sensitive.

In several investigations the photochemical decomposi-

tion of oxalic acid sensitised by uranyl salts has been recommended as a useful method of comparing the ultra-violet intensities of different light sources. First investigated by Mathews and Dewey,[7] the conditions for successful working have been standardised by Anderson and Robinson [8] and by Moss and Knapp.[9]

Anderson and Robinson's Arrangements.—The following stock solutions are made up :

(*a*) 6·3 grams crystalline oxalic acid ; 4·27 grams of uranyl sulphate, $UO_2SO_4.3H_2O$, made up to 1,000 c.c.

(*b*) N/10 potassium permanganate standardised against oxalic acid.

25 c.c. of (*a*) are placed in a vessel of fused quartz and exposed to a source of ultra-violet light for a definite time at a definite distance and then titrated against (*b*). A blank titration is carried out on the unexposed solution. The amount of decomposition effected by the light is found by difference and expressed in terms of oxalic acid or in permanganate. The quantity of energy corresponding with a given amount of chemical change can also be determined if necessary (see the original paper). The reaction is simple, it proceeds with a moderate velocity, is reproducible, and is moreover sensitive to the whole of the ultra-violet radiation from the mercury arc and is not affected by visible and infra-red rays. The temperature coefficient of 1·035 for a 10-degree interval is, as would be expected for a purely photochemical change, very small.

As an example of the results given by the test the following figures obtained by Mr. Gillam may be quoted :

Lamp : fairly new Hewittic. Distance : 6 inches. Time : 2 hours. Screen : none. Titration : 12·3 c.c. of 0·094 permanganate correspond with the oxalic acid decomposed in the irradiation.

A series of screening experiments gave the following relative results :

	Hewittic lamp.	K.B.B. lamp.
No screen	100	100
Vitaglass screen	39·2	41·7
Window-glass screen	24·6	28·9

The spectrum of the oxalic acid-uranyl salt solution exhibits a by no means negligible amount of absorption in the region 300–380$\mu\mu$. This fact is in agreement with the results of the screening experiments, since 25–30 per cent of the decomposition occurs with rays longer than 325$\mu\mu$ and about 40 per cent. with rays on the same side of the vitaglass limit at 275$\mu\mu$.

The region associated with the therapeutic action of light contributes about 20 per cent. to the decomposition. Experiments were tried using sunlight as the source of light, and the following figures indicate the results obtained on three different days :

I.	25 c.c. of solution, exposure	1 hour	9·55 c.c.	0·094 $KMnO_4$
II.	,, ,, ,,	3 hours	19·5	,, ,,
III.	,, ,, ,,	2 hours	20·3	,, ,,

The effect of screens was as follows :

No screen : vitaglass screen : glass screen=100 : 86·7 : 67·5.

The reaction thus responds readily to the superior transmission of vitaglass.

Moss and Knapp's " Uroxameter." [9]—The test solution consists of a mixture of 20 c.c. of a 2 per cent. solution of crystalline oxalic acid in water, 5 c.c. of a 1 per cent. solution of uranyl acetate crystals in water, and 20 c.c. of distilled water. This is placed in a circular flat-bottomed vessel 10 cm. in diameter with vertical glass walls 8 cm. high. The walls are painted on the outside with one coat of red paint and three of white, so that the interior of the vessel appears red and the passage of light through the sides is prevented, while the white paint serves to reflect heat from the outside. On the top of the cell can be fitted a gas-tight lid of fused transparent silica. The whole is placed at a distance of 6½ inches below the lamp to be tested, and is rotated by means of a table at 5–6 revolutions per minute. Part of the test solution is titrated against N/10 permanganate for purposes of standardisation. 45 c.c. of the test solution are then exposed to the light for half an hour

and the solution is then titrated, so that the amount of decomposition may be obtained by difference.

The uranyl acetate solution should not be allowed to stand for more than a fortnight, and if precipitate should be formed a fresh solution will be needed. In later papers [10] the authors concede that for comparative work the method may be considerably simplified as regards manipulation, and an alternative test solution containing twenty times as much uranyl salt is suggested for use in testing carbon arcs. The writer is not convinced that the "twenty strength" solution represents an advance, as the absorption spectrum of this solution is vastly different from that of the Uroxameter reagent, and, as will be seen, the spectral sensitivity of the new reagent is thereby shifted considerably in the direction of the visible.

Moss and Knapp obtained some very interesting results with their original method, and the following example may be quoted. Using a new quartz-mercury vapour lamp, the output as measured by the decomposition of oxalic acid fell off with great rapidity.

Time of running.	Percentage of oxalic acid decomposed.
30 minutes	62·1
9 hours	55·3
18 hours	49·1
29·5 hours	40·7
48 hours	32·8
68 hours	29·05

While the authors do not claim this lamp to be typical, it must be admitted the results of tests carried by Gillam and the writer reveal a similarly disquieting state of affairs.

Moss and Knapp also used the method to test the transparency of different glasses to ultra-violet rays.

Glass.	Thickness.	Percentage of ultra-violet transmitted.
Silica	0·110 inch	85·7
Vitaglass	0·065 ,,	24·4 and 20·8 on different tests.
Window-glass	0·082 ,,	3·1
"Calorex" glass	0·208 ,,	nil
Non-actinic glass	0·238 ,,	0·4

These results are entirely in agreement with the claims of the manufacturers of the proprietary glasses.

To obtain comparative results with the three oxalic acid-uranyl actinometers (namely: Anderson and Robinson's oxalic acid-uranyl sulphate solution; Moss and Knapp's "Uroxameter" solution; Moss and Knapp's 20 strength solution) Gillam and Morton [11] modified the precedure of Moss and Knapp so far as to dispense with the flat-bottomed dish and used in its place a 6-inch × ¾-inch clear quartz test-tube.

Three similar quartz test-tubes containing the three solutions were exposed for 2 hours at 12 inches from a Kelvin Bottomley and Baird quartz-mercury vapour lamp. 25 c.c. of each solution were titrated before and after exposure. The decompositions were as follows:

Anderson and Robinson solution	= 7·7 c.c.	0·1046 N $KMnO_4$
Moss and Knapp's Uroxameter solution	= 5·32	ditto.
,, ,, 20 strength solution	= 7·3	ditto.

The three tubes containing the three solutions were then exposed for a definite time, and at a definite distance, first under vitaglass and then under window-glass, the decomposition in each case being determined by titration with $KMnO_4$.

Expressing the decomposition in each case under vitaglass and window-glass as the percentage of decomposition with an unscreened quartz tube they obtained the following results with a K.B.B. quartz-mercury vapour lamp (average of three sets of experiments):

	Quartz.	Vitaglass.	Window-glass.
Anderson and Robinson's solution	100	42·3	27·3
Moss and Knapp's "Uroxameter" solution	100	30·8	13·3
Moss and Knapp's "20-strength" solution	100	51·6	27·1

A comparison may now be made of the results obtained with the different methods:

					Oxalic acid decomposition.				
	Acetone-methylene blue test.		Nitrate photolysis.		Anderson-Robinson.		Moss and Knapp uroxameter.		Moss and Knapp "20-strength."
	Hewittic.	"K.B.B."	Hewittic.	"K.B.B."	Hewittic.	"K.B.B."	Hewittic.	"K.B.B."	"K.B.B."
No screen ..	100	100	100	100	100	100	100	100	100
Vitaglass screen ..	10·7	13·0	1·9	2·38	39·2	42·3	31·0	30·8	51·6
Window-glass screen ..	4·76	6·48	0·325	0·67	24·6	27·3	12·8	13·3	27·1
Remarks ..	Averages of many observations:						1 Set	av'ge.	1 Set

The table indicates the amount of reaction which occurs in each case with the value for the unscreened reaction taken as 100. The values in the first horizontal line of the table are, of course, not comparable. It will be noted that the figures for the screened experiments with the lamp are uniformly higher for the K.B.B. lamp than the corresponding figures for the vacuum burner, indicating a slight difference in spectral sensitivity, in the sense of a larger accumulation in the middle and near ultra-violet regions. The following table makes clear the effect of wave-length:

Method.	Mercury vapour lamp used.	Rays shorter than 275$\mu\mu$ app.	Rays between 275 and 325$\mu\mu$ app.	Rays longer than 325$\mu\mu$.
Nitrate method (Buffered KNO_3)	K.B.B.	97·6	1·71	1·71
	Hewittic	98·1	1·57	0·33
Carbon tetrachloride	K.B.B.	100	nil	nil
Acetone-methylene blue gauge	K.B.B.	87	6·5	6·5
	Hewittic	89	6·3	4·7
Anderson and Robinson's oxalic acid	K.B.B.	57·7	15·0	27·3
	Hewittic	60·8	14·6	24·6
Moss and Knapp's "Uroxameter" solution	K.B.B.	69·2	17·5	13·3
	Hewittic	69·0	17·2	12·8
Moss and Knapp's "20-strength" solution	K.B.B.	48·4	24·5	27·1

From this table it will be seen that the nitrate and carbon tetrachloride methods are most fitted to measure the bactericidal rays. The three oxalic acid-uranyl salt solutions, on the other hand, appear to give the biggest reaction among the actinometers examined with the middle ultra-violet rays. This region is approximately the same as that covered by the rays active in light therapy.

The following table indicates the results of comparative experiments with different light sources:

	Hewittic old lamp.	Hewittic new lamp.	"K.B.B." atmospheric lamp.	Iron-nickel arc.
Acetone-methylene blue	2·6	7	20·48	1·5 units.
Oxalic acid-uranyl sulphate.. ..	3·1	8·8	20·4	1·18 c.cm. 0·094N oxalic acid.
Nitrite photolysis..	6·4	25·6	74·8	5·2 c.cm. N/5,000 nitrite.

Time 4 hours. Distance 12 inches.

The table may be expressed in terms of the percentage effect with the "K.B.B." lamp.

	K.B.B.	Hewittic New.	Hewittic Old.	Fe-Ni-arc.
Acetone-methylene blue	100	34·6	12·7	7·3
Oxalic acid-uranyl sulphate	100	43·2	15·2	5·8
Nitrate photolysis ..	100	34·2	8·5	7·95

It might be thought from these results that the K.B.B. lamp is by far the best source. Such a conclusion would, however, not be warranted without considering the behaviour of the different sources over the full period of normal use. Data of this kind are not available for strictly comparable conditions. We do not even know whether the cleaning of an atmospheric burner by removing the mercury and

washing with nitric acid (an operation impossible with the vacuum burner) results in a complete recovery of the original output.

The deterioration of a K.B.B. atmospheric burner which had been running for 1,100 hours spread over the period June to December may be gauged from the following ratios :

	June.	December.
(1) By nitrate method	100	10·6
(2) By oxalic acid (Anderson-Robinson)	100	28·8
(3) Acetone-methylene blue	100	23·8

The oxalic method will be seen to agree well with the results of the acetone-methylene blue test in this case. It must, however, be emphasised that the average of a number of readings, each extending over at least two hours, is necessary if quantitative data are to be obtained from the methylene blue test.

The deterioration of quartz-mercury lamps has also been studied by Coblentz,[12] who records that the percentage of the total radiation which is below 450$\mu\mu$ decreases from an initial value of 70 to 50 after 1,000–1,500 hours' use. Aston [13] states that after 200 hours' use all lines in the ultra-violet were obliterated except those at 313 and 366$\mu\mu$. Coblentz, Long and Kabler [14] determined the intensity by means of a thermopile, and by using a filter to isolate the ultra-violet rays were able to show that the total radiation as well as the ultra-violet part fell to about 50–30 per cent. after 1,000–1,500 hours' use.

Nelson [15] measured the output of a mercury lamp by means of the ionising effect on a charged zinc plate, a method sensitive only to rays shorter than 300$\mu\mu$. No decrease was noticed for 500 hours, but after 1,800 hours the emission had fallen to about 50 per cent.

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SECTION IV.—PHOTOCHEMICAL REACTIONS

Photochemistry of Water and Hydrogen Peroxide.— Hydrogen and oxygen combine under the influence of ultra-violet rays from a quartz-mercury vapour lamp.

Thiele [1] tried (*a*) moist gases, (*b*) gases dried by means of concentrated sulphuric acid, and (*c*) gases dried somewhat "intensively" by contact with phosphorus pentoxide for eighteen days. Combination occurred in all three cases, but the reaction was less rapid with the moist gases.

Dickinson [2] obtained combination at ordinary temperatures in the presence of mercury. The very strong resonance line occurring at 2,536 Å. in the spectrum of the quartz lamp is absorbed by the mercury in the reaction vessel. This absorption brings into being "excited" mercury atoms, which collide with hydrogen molecules and part with the energy acquired in the excitation process. This energy causes dissociation of hydrogen molecules into atoms which are then in a very reactive condition.

$$Hg + \text{resonance radiation} \rightarrow Hg^*$$

$$\underset{\text{inelastic collision.}}{Hg^* + H_2} \rightarrow \underset{\text{normal atom.}}{Hg + 2H}$$

Downes and Blunt [3] found that hydrogen peroxide was decomposed in glass bottles exposed to the light.

Kernbaum [4] claims to have observed the decomposition of water by means of ultra-violet rays. Distilled water, free from air and placed in quartz vessels, evolves gas after a few hours' exposure to sunlight. Hydrogen peroxide

was detected in the absence of air, and was found to be present in larger amount when air was not excluded.

Tian [5] found that pure water is only decomposed by very short wave-length ultra-violet rays, whereas hydrogen peroxide is susceptible to the action of much longer waves. It frequently happens that products formed by rays shorter than, say, $220\mu\mu$ are decomposed by longer wave-lengths, both ozone and hydrogen peroxide being good examples of this phenomenon. In the presence of dissolved oxygen the reactions

$$2H_2O \rightarrow 2H_2+O_2, \quad 2H_2O \rightarrow H_2O_2+H_2$$
$$3O_2 \rightarrow 2O_3, \quad 2H_2O_2 \rightarrow 2H_2O+O_2$$
$$H_2O_2+O_3 \rightarrow H_2O+2O_2$$
$$H_2O+O \rightarrow H_2O_2$$

can all occur. Hydrogen peroxide can only be formed by rays shorter than $190\mu\mu$, and in order to secure a good yield the solution should be protected from light of longer wave-length.

The ultra-violet absorption spectrum of hydrogen peroxide has been measured by Rosanoff [6] and by Henri and Wurmser [7] with the following results:

Wave-length in $\mu\mu$.	Molecular extinction coefficient.
311	0·422
280	3·0
254	20·0
230	75·0
210	127·0
206	127·0

The latter authors also showed that in the photochemical decomposition of the peroxide by means of monochromatic light:

(*a*) The reaction is monomolecular.

(*b*) The rate of decomposition varies directly as the concentration.

(*c*) For each wave-length used the rate of decomposition is proportional to the incident energy.

The rate of decomposition is retarded by the presence of either acid or alkali, the latter showing the greater

effect. Somewhat similar results were obtained by Miss Kornfeld.[8]

The decomposition of hydrogen peroxide can be inhibited by the addition of various organic compounds, a fact which is made use of in various proprietary preparations rich in the peroxide. Mathews and Curtis [9] examined this question in detail and the table summarises their results :

PHOTO-DECOMPOSITION OF HYDROGEN PEROXIDE.

Accelerates decomposition.	No action.	Slight retarding action.	Powerful retarding action.
Barium nitrate	Acetamide Carbamide Boric acid Barium chloride	Sodium chloride Potassium chloride Potassium nitrate Sulphuric acid Phosphoric acid Tartaric acid Acetic acid	Benzoic acid Calcium hydroxide Sodium hydroxide Barium hydroxide

Anderson and Taylor [10] tested the inhibitory effects of a large number of organic compounds. They also tried the effect of using screens to limit the range of ultra-violet wavelengths concerned in the reaction. It was found in most cases that the absorptive power of the added compound accounted to some extent for the inhibition, and in certain cases, notably benzene, acetophenone, and benzophenone, a close parallelism between inhibition and absorption spectra was observed. The table on p. 73 summarises the results obtained with the inhibitors present in the hydrogen peroxide solutions.

The values may be interpreted as follows: 80–100, extremely weak or no inhibition; 50-80, weak inhibition; 30–50, moderate inhibition; 20–30, fairly strong inhibition; 10–20, strong inhibition; 0–10, very strong inhibition.

The inhibitors act more efficiently when in the hydrogen peroxide solution than when employed as screening solutions. The explanation of this effect possibly lies in the ability of one quantum to decompose more than one molecule.

REGIONS OF WAVE-LENGTH.

Substance.	Conc. M.	to 2,000	to 2,650	to 2,930	to 3,050 Å.
Acetic acid ..	0·005	75	100	100	100
Phenylacetic acid ..	0·001	13	45	80	100
Hydrocinnamic acid	0·003 app.	12	40	70	100
Benzoic acid ..	0·005	9	—	—	100
Ethyl acetate ..	0·005	100	100	100	100
Ethyl benzoate ..	0·001 app.	14	50	80	100
Ethylphenyl acetate	0·001 app.	17	70	85	100
Ethyl cinnamate ..	0·0002 app.	25	45	65	100
Methyl oxalate ..	0·005	10	20	35	70
Methyl benzoate ..	0·005	9	—	—	—
Ethylamine ..	0·005 app.	5	0	0	0
Aniline	0·005	7	0	0	0
Benzylamine ..	0·005	8	0	0	0
Acetamide	0·005	65	100	100	100
Benzamide ..	0·003	9	—	—	—
Acetanilide ..	0·0001	60	100	100	100
Ethyl alcohol ..	0·005	35	35	35	35
Phenol	0·002	0	0	0	0
Benzyl alcohol ..	0·0033 app.	8	25	40	40
Acetone	0·005	70	60	55	50
Acetophenone ..	0·0002	11	40	65	100
Benzophenone ..	0·0001	45	60	100	100
Benzene	0·005	20	—	70	—
Quinine hydro-chloride	0·0002	9	20	10	0
Quinine salicylate ..	0·0002	4	0	0	0

The available evidence on the problem of inhibition is conflicting, but the main facts appear to be as follows:

(*a*) Hydroxyl ions act about 25 times as efficiently in retarding the decomposition as the same number of hydrogen ions;

(*b*) Hydrogen peroxide acts as a weak acid,

$$HOOH \rightleftharpoons H^{+} + HOO^{-}$$

so that added hydrogen ions will decrease the dissociation of the peroxide;

(*c*) Inhibition does not occur as a result of the addition of the following ions:

$$SO_4'', ClO_4', NO_3', Ca^{\cdot\cdot}, Ba^{\cdot\cdot}, Sn^{\cdot\cdot}$$

(*d*) The inhibition varies with the concentrations of peroxide or added substance and with the wave-length of the incident light;

(*e*) The absorption spectrum of the inhibitor plays an important part ;

(*f*) The Einstein Law (see p. 4) is not obeyed, since one quantum may decompose as many as 80 molecules of peroxide.

The Oxygen-Ozone System.—It is a well-known fact that the air in the neighbourhood of *new* quartz-mercury lamps smells of ozone. It is also usually observed that the indications of ozone formation grow less and less as the period for which the lamp has been in use increases.

These results find an explanation in the fact referred to on p. 28, that the ageing of quartz lamps is accompanied by a pronounced decrease in the transparency of quartz to very short-wave radiation. Lenard (*Ann. Physik.*, 1900, **1**, 486) has indeed shown definitely that the reaction

$$3O_2 \rightarrow 2O_3$$

requires rays of wave-length less than $200\mu\mu$. It will be remembered that in discussing the effect of the silent electric discharge on the system carbon dioxide-water, the conclusion was reached that very short-wave radiation was at least partially responsible for the reactions which occur.

The ozonising action of the silent electric discharge also supports this mechanism. Warburg and Regener [11] have shown that the ozone itself may also decompose in the discharge.

Ozone has been shown by Fabry and Buisson [12] and others to exhibit marked selective absorption with a maximum at $247–248\mu\mu$. The absorption has been found to extend as far as $316\mu\mu$ (Ledanburg and Lehmann) even when the gas is present in low concentrations.

The oxygen-ozone system may, therefore, be expressed by the equation

$$3O_2 \underset{\text{light}<316\mu\mu}{\overset{\text{light}<200\mu\mu}{\rightleftharpoons}} 2O_3$$

This simple method of formulating the photochemical reaction helps to make clear the results of Goldstein.[13]

This author passed the discharge from an induction coil through an exhausted quartz tube and obtained an intense reaction for ozone in the surrounding air, provided the pressure in the tube was low. Now, if the effect is due to short-wave ultra-violet rays the failure to obtain high yields of ozone at moderate pressures finds a ready explanation in the absorptive power of air for these extremely short rays. Goldstein then took a Geissler tube containing oxygen at a few cm. pressure, and cooled at one end by means of liquid air. It was then subjected to the action of the discharge from an induction coil. Ozone was formed, and as the treatment was continued all the oxygen was converted, since the ozone formed was removed from the gaseous phase by liquefaction. Potter [14] describes a method for preparing ozone photochemically. A quartz-mercury lamp is enclosed by a double-walled sleeve, and a current of air is passed between the lamp and the inner wall, and a current of water through the annular space. The inner wall is silvered. Fischer and Braehmer [15] describe a method similar in principle.

Rideal and Kunz [16] ably review the methods by which ozone can be prepared and describe experiments on the reactions occurring when dry oxygen is passed through a corona discharge.

Noyes and Kassel [17] review the subject of the decomposition of ozone. The thermal decomposition of ozonised oxygen in the absence of catalysts is a second order reaction with respect to ozone concentration. The reaction follows approximately the equation

$$\log k = -5{,}700/T + 14{\cdot}939$$

Perman and Graves [18] found that in the presence of glass-wool or tubing the reaction occurred largely at the surface. Clarke and Chapman,[19] however, found the reaction to occur almost wholly in the gaseous phase.

It is agreed that the photochemical decomposition is a first order reaction except for very thin layers. Weigert [20] observed an apparent order of 1·4 with thicknesses of 5 mm.

Inactive gases retard the photochemical decomposition. Griffith and his collaborators have thrown much light on the problem of the photo-decomposition, and their results may be briefly given.[21]

(*a*) Ozone is decomposed by visible light. The regions 510–615$\mu\mu$ and 670–760$\mu\mu$ are particularly effective.

(*b*) The absorption spectrum of ozone in the visible shows maxima in the effective regions, indicating a correlation between photochemical efficiency and extinction coefficient.

(*c*) The decomposition is accelerated in the presence of hydrogen, and very complex reactions occur.

The effect of hydrogen may be due to local heating as a result of the reaction:

$$O_3+H_2 \rightarrow H_2O+O_2$$

(Weigert and Bohm), but it is more probable that the first product is activated water, H_2O^*, which may then lose its extra energy by inelastic collisions:

$$\left.\begin{array}{ll} & H_2+O \rightarrow H_2O^* \\ \text{or} & H_2+O_3 \rightarrow H_2O^*+O_2 \end{array}\right\} \text{both exothermic reactions.}$$

Griffith and McKeown[22] have argued on the basis of the effects of indifferent gases that the visible light reaction is best formulated as:

$$O_3+h\nu \rightarrow O_3^*$$
$$O_3^*+O_3 \rightarrow \text{complex}$$
$$\text{complex} \rightarrow 3O_2 \text{ (catalysed by inert gases).}$$

The intermediate complex provides a means for explaining the catalytic effect of indifferent gases. The photochemical decomposition of ozone will be seen to be a very complicated question of great theoretical interest, but any further discussion would be out of place here and the reader is referred to the original memoirs.

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Reduction of Carbon Dioxide.—The reduction of carbon dioxide is the most important step in plant photosynthesis. The conversion of water and carbon dioxide to sugars represents a very large amount of energy, and the method by which this change occurs remains obscure in spite of much investigation.

Willstätter and Stoll proved for the leaf that within very narrow limits the volume of oxygen transpired is equal to the volume of carbon dioxide absorbed. This result is in conformity with the formulation

$$nCO_2+nH_2O \rightarrow nCH_2O+nO_2$$

At one period a photocatalytic mechanism involving the plant pigments carotin, xanthophyll, chlorophyll-A, and chlorophyll-B was invoked, but this view has receded from favour owing to the demonstration that the rate of assimilation changes but little when the concentration of chlorophyll is varied over a somewhat wide range. The importance of the rôle of the pigments is still further reduced by experiments of Willstätter and Stoll, and of Kremann and Schniderschitsch, which show that although chlorophyll does adsorb carbon dioxide to some extent, the amount of adsorption is negligible in comparison with that which occurs with green leaves, namely 150–170 molecules per molecule of chlorophyll. The CO_2/O_2 ratio observed by Willstätter and Stoll would appear to indicate that formaldehyde in

some form or another should be the primary product of phytosynthesis. The fact that the presence of formaldehyde in green leaves has never been unequivocally demonstrated shows that if formed it must occur in a very reactive or unstable condition.

It is possible that phytosynthesis occurs as a heterogeneous reaction of the type suggested by Ostwald. This author regards globulin as capable of forming globulin carbonate or a globulin-carbon dioxide adsorption complex. Lipoid peroxides are regarded as playing an important rôle and the seat of the significant reaction is the globulin–lipoid peroxide interface. Formaldehyde and oxygen are, it is thought, formed under these conditions.

Another view is expressed as follows :

$$CO_2+H_2O \rightarrow \underset{\text{formic acid peroxide}}{H\overset{\overset{\displaystyle O}{\|}}{C}-O-OH} \xrightarrow{H_2O} H.CHO+\underset{\text{or } O_2}{H_2O_2}$$

Another possibility is found in the reactions

$$\left.\begin{array}{l} CO_2 \rightarrow CO+O \\ H_2O \rightarrow H_2+O \end{array}\right\} CO_2+H_2O \rightarrow H.CHO+O_2$$

or

$$CO+H_2O \rightarrow H.COOH \rightarrow CO_2+H.CHO$$

A variety of step mechanisms have thus been suggested on more or less plausible grounds.

We may first consider some ordinary chemical reactions. Carbonic acid has been converted to formic acid by sodium amalgam (Ballo [1]). The equilibrium

$$CO_2+H_2 \rightleftarrows CO+H_2O \rightleftarrows HCOOH$$

has been studied by Bredig and Carter [2] at different pressures and in the presence of different catalysts, but no indications were obtained of the formation of formaldehyde. Fenton [3] accomplished the direct reduction of carbonic acid to formaldehyde by the use of metallic magnesium. The presence of weak alkalis favours this reduction, probably owing to formation of bicarbonates. Formic acid may also be reduced to formaldehyde by means of magnesium. The effect of the silent electric discharge on the system

carbon dioxide-water is of great interest, since the reactions which occur are probably photochemical in at least the initial stages. The energy of the discharge is converted partially into quite short wave-length ultra-violet light, since the ozonisation process occurs either with the silent electric discharge or with ultra-violet rays about 200$\mu\mu$ in wave-length. Losanitsch and Jovitschitsch [4] and Löb [5] indicate that all of the following reactions can occur in the silent discharge:

$$2CO_2 \rightarrow 2CO + O_2 \qquad 3O_2 \rightarrow 2O_3$$
$$CO + H_2O \rightarrow H.COOH$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$2H_2 + 3O_2 \rightarrow 2H_2O_2 + O_2$$
$$H_2 + CO \rightarrow H.CHO$$

The balance between these various possibilities depends to a large extent on the amount of water vapour present. Glycollic aldehyde was also isolated by Löb as a result of the interaction between carbon monoxide and hydrogen. The view that the reactions in the silent electrical discharge are photochemical is at any rate not weakened by the fact that α-particles, β-particles, and the corona discharge (R. W. Lunt [6]) (high-frequency alternating currents) do not bring about the formation of formaldehyde or formic acid.

The photochemical mechanism is, on the other hand, definitely supported by the reproduction of many of the reactions when short-wave ultra-violet light is used.

Kernbaum [7] obtained hydrogen peroxide and hydrogen by illuminating water for ten hours, and Thiele [8] confirmed the formation of hydrogen peroxide, whilst Coehn [9] observed an equilibrium corresponding with the calculated thermal equilibrium at 1,250°.

Coehn and his collaborators have shown that dry carbon dioxide is decomposed by short-wave ultra-violet light. The effective range may be gauged from the absorption measurements of Kreuler.

Wave-length in $\mu\mu$.	Per cent. absorption by CO_2.
200	1·8
193	4·0
186	13·6

The reaction:

$$\text{dry } CO_2 \underset{}{\overset{\text{light}}{\rightleftarrows}} CO + O_2$$

was realised by Herchefinkel,[10] and Berthelot and Gaudechon [11] supplied confirmation. The presence of an oxygen acceptor was shown to favour the decomposition. The reactions:

$$CO + H_2 \xrightarrow{\text{light}} H.CHO \xrightarrow{\text{light}} \text{polymers}$$

were shown to proceed readily, but the reaction $CO_2 + H_2O \rightarrow H.CHO + O_2$ could not be carried out except when hydrogen was also present. Usher and Priestley,[12] on the other hand, record positive tests for formaldehyde, using quartz vessels, carbon dioxide, and water. There is little doubt, however, that these results are unreliable, owing to contamination of the water which was used in open dishes. Stoklasa and Zdobnicky [13] found:

(1) No formaldehyde and no sugars as a result of irradiating water and carbon dioxide.

(2) A positive test for formaldehyde when aqueous carbon dioxide was subjected to short-wave ultraviolet light in the presence of nascent hydrogen and potassium hydroxide.

The mechanism is regarded as:

$$2KHCO_3 \xrightarrow{\text{light}} K_2CO_3 + H.COOH + O$$
$$HCOOH \xrightarrow{\text{light}} H.CHO + O$$
$$n.HCHO \rightarrow (CHOH).n$$

Stoklasa has isolated a hexose, but has not shown that the reaction:

$$H.COOH \xrightarrow{\text{light}} H.CHO + O$$

can be carried out.

Baly, Heilbron and Barker [14] claimed to have shown that carbon dioxide and water give formaldehyde on exposure to light, in accordance with the equation:

$$CO_2 + H_2O \xrightarrow{\text{light of W. L.} < 220\mu\mu} HCHO$$

whereas the polymerisation takes place with longer wavelengths near $290\mu\mu$. In any case, the amounts of formaldehyde detected were so small as to leave the possibility of

contamination quite an open one. Baly's subsequent experience points to a hexose as the first product.

The formaldehyde question has been investigated by various other authors, mostly with negative results.

Spoehr,[15] in a very exhaustive and careful investigation, varied :

(1) The type of quartz-mercury vapour lamp.

(2) Temperature.

(3) Pressure of carbon dioxide.

(4) Time and distance of exposure.

Formaldehyde was never definitely obtained. Coehn and Sieper [16] (1916), Chadwick, Chapman and Ramsbottom,[17] and Baur and Rebmann,[18] likewise obtained negative results. Porter and Ramsperger [19] subjected the matter to what for most questions would have been a decisive test.

"In every run where the illuminated gas came in contact with rubber tubing, sealing wax, de Khotinsky cement, or stop-cock grease, small quantities of formaldehyde were obtained, but the results were never quantitatively reproducible. The entire apparatus was then reconstructed, using quartz-to-glass seals, conductivity water, and *pure* carbon dioxide. No trace of formaldehyde or reducing sugars was obtained after 36–60 hours' exposure using *new* quartz vessels."

Porter and Ramsperger conclude : "These experiments compel us to believe that if formaldehyde is formed from carbon dioxide and water alone, under the influence of ultra-violet radiation, the reaction is reversible, and the ordinary mercury arc provides the energy required to decompose formaldehyde as fast as it is formed. . . . The next experiment in this field must be with monochromatic ultra-violet light."

Dr. R. W. Riding and the author have studied the possibility of photosynthetic formation of formaldehyde (unpublished work). The first line of investigation was to see whether formaldehyde could be obtained in a homogeneous gaseous system. The results of this and similar work may be summarised.

SYSTEM: WATER VAPOUR—CARBON DIOXIDE

Per cent. water vapour.	Test for formaldehyde.	Observers.
40	Negative	Coehn and Sieper
25	,,	,, ,,
4	,,	Porter and Ramsperger.
1·33	,,	Riding and Morton.
0·133	,,	,, ,,

The system: hydrogen—carbon dioxide gave negative tests for formaldehyde in all cases, whether the gases were moist or dry. Riding and Morton also obtained negative tests for the system carbon monoxide—water vapour when the percentage of the latter was 1·33 and 0·133. The entire apparatus was of glass, and the only joints used were glass-to-quartz, and were lubricated with water only. No greased taps were used. The uniformly negative results in the homogeneous vapour state established confidence in the technique, and it was therefore surprising that numerous positive tests were obtained when liquid water was present in the bottom of the quartz vessel. It was then thought that the formaldehyde might have been obtained by the exposure of a fine mist or spray. Two experiments were therefore performed, one in which a coarse spray was obtained by fine jets, and the other by using an atomiser. The former gave negative tests whilst the latter gave some negative and some positive results, which were independently confirmed by Messrs. Davies and Johnson under Professor Baly's direction. In considering these experiments the work of Zenghelis [20] was recalled. This author conducted a series of experiments with the view of attempting to explain the activity of gases in the presence of colloids. He assumed that the activity of the gas was due to its extremely fine state of subdivision, and hence examined the properties of gases mechanically broken up into fine bubbles by forcing them through filter thimbles. Hydrogen, used in this way, possessed abnormal reducing powers, since it reduced mercuric chloride, potassium chlorate, potassium nitrate, and carbon dioxide. Oxygen likewise showed abnormal oxidising power, and carbon monoxide abnormal reducing power. The reduction of carbon monoxide to formaldehyde is of considerable interest, as although it

might be considered as a "dark" reaction, the yield of formaldehyde or sugars is greatly increased either by bright sunlight or ultra-violet light. From this research no reason could be found why other gases should not be activated in a similar manner, so experiments were tried in which carbon dioxide was forced through a filter-paper thimble and a porous filter tube of the Pasteur-Chamberland type. In both cases, using a quartz tube and ultra-violet light, a very good yield of formaldehyde was obtained, though using uviol glass sleeves little or none of this substance could be detected. These results, therefore, offer some explanation of the anomalous results obtained earlier.

The study of the rôle of surface activity in photochemical reactions has been actively pursued in Baly's laboratories, and it has now become clear that formaldehyde is not the *first* product of photosynthesis. Whatever the true explanation of the work of Riding and Morton may be, the experiments are not without interest.

Effect of Ultra-Violet Light on Formaldehyde.—By the kindness of Professor E. C. C. Baly it is possible to give a brief account of studies carried out by him over a period of years with various collaborators.

A 40 per cent. formalin solution is placed in a tank of the type indicated in Fig. 17, and exposed to the continuous action of ultra-violet rays from four quartz-mercury vapour lamps of the vacuum type for a period of a month. The solution always contains excess of calcium carbonate in suspension, and stirring is carried on the whole time, as well as cooling by means of water coils to maintain a temperature not greater than 30° C. At the end of four weeks the solution is evaporated down *in vacuo* in the presence of calcium carbonate at a temperature not exceeding 50° C. The result is a syrup containing calcium salts. On addition of alcohol the syrup goes into solution and calcium salts are precipitated. It has been shown that the salts consist of 80 per cent. calcium formate, 5-6 per cent. calcium glycollate, and some 15 per cent. of a complex mixture. The syrup contains calcium salts soluble in alcohol. The alcohol

is evaporated off and the calcium content of the residue estimated. The syrup is now dissolved in water and an

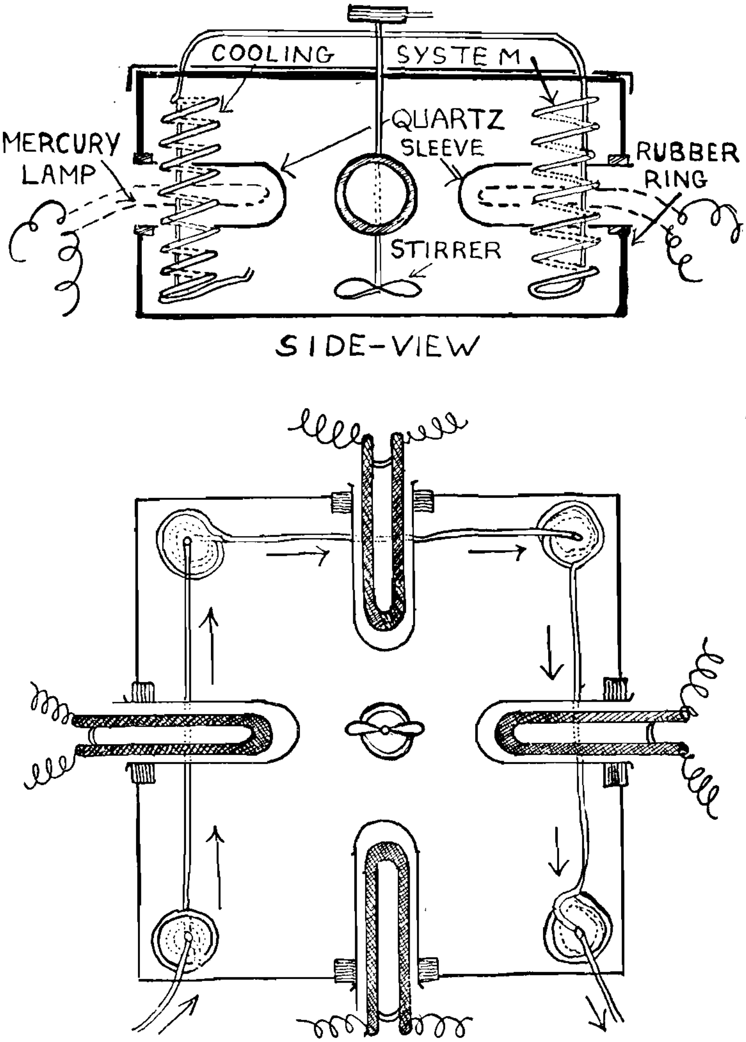

FIG. 17.—Photosynthesis tank designed by Professor E. C. C. Baly.

amount of zinc sulphate exactly equivalent to the lime content is added, so that the calcium is precipitated almost quantitatively on standing. The filtered solution is again

evaporated down to carefully controlled bulk and chloroform is added. The material is then divided into two fractions soluble and insoluble respectively in chloroform. The soluble portion contains glycol, glycerol, and pentaerythritol amongst other substances. The insoluble portion contains all the reducing sugar, and may be obtained as a very fine syrup. Glycollic acid, hexonic acids, *d*- and *l*-erythronic acids, and a penta-methyl-hexose have been obtained, using this syrup as a starting-point.

These results represent a very considerable achievement, which can only be adequately appreciated by those conversant with the great difficulties involved in working up large quantities of more or less decomposed formalin to the stage of isolating pure crystalline sugar derivatives.

The study of photosynthesis has entered on a new phase with the recent (September, 1927) publication of three important and suggestive papers by Baly and his collaborators.

In the first, Baly, Davies, Johnson and Shanassy [22] discuss the action of ultra-violet light on carbonic acid. It will be recalled that Baly, Heilbron and Barker [14] found irradiation to cause the formation of traces of formaldehyde in pure aqueous solutions of carbonic acid, whilst Moore and Webster [21] regarded a catalyst such as colloidal ferric or uranium hydroxide as essential.

Baly's view may be shown diagrammatically as follows :

$$H_2CO_3 \xrightarrow{\text{light}} H_2CO_3 \text{ (activated)}$$
$$H_2CO_3 \text{ (activated)} \rightarrow H.COH \text{ (activated)} + O_2$$
$$HCOH \text{ (activated)} \rightarrow H.CHO \text{ (ordinary)}$$
$$HCHO \xrightarrow{\text{light}} H.COH \text{ (activated)}$$
$$x.H(COH) \rightarrow \text{carbohydrate.}$$

In the latest work the above scheme is abandoned and replaced by

$$H_2CO_3 \xrightarrow{\text{light}} H_2CO_3 \text{ (activated)} \rightarrow H.COH + O_2$$
$$xH.COH \rightarrow \text{carbohydrate}$$
$$\text{carbohydrate} \xrightarrow{\text{light}} \text{formaldehyde (H.CHO).}$$

The action of ultra-violet light on carbonic acid is probably the establishment of a photostationary state represented by

$$6H_2CO_3 \rightleftarrows C_6H_{12}O_6 + 6O_2$$

in which the equilibrium concentration of carbohydrate is very small. "In the presence of oxidisable impurities the reaction would proceed from left to right with the formation of a definite amount of carbohydrate which would be photochemically decomposed to formaldehyde." The negative results of Porter and Ramsperger are, it is suggested, due to the exclusion of all trace of oxidisable impurity.

In order to establish the reality of the photostationary state, experiments were carried out on the irradiation of carbonic acid in conductivity water in quartz vessels. Feder's test showed that an aldehydic body not formaldehyde was formed in the light, whilst control experiments showed that pure water in the light and carbonic acid in the dark gave negative results.

Having proved the reality of the photostationary state, the next step was to shift the equilibrium in the direction of a larger yield of carbohydrate. Bannister had observed that pure iron in the presence of carbonic acid and in the absence of oxygen rusted rapidly on exposure to ultra-violet light. This fact suggested to Baly "the possibility that carbohydrates are formed by the action of the ultra-violet light on the carbonic acid, and that the ferrous bicarbonate takes up oxygen with the formation of ferric hydroxide." This explanation was tested experimentally, and found to be supported by the fact that organic compounds exhibiting reducing properties (Benedict test) were formed at the same time as ferric hydroxide. It was noticed that the hydroxide was formed largely on the walls of the quartz reaction vessel and on the surface of the rods of Swedish iron used on the experiments. This observation (supported by the work on surfaces already described) led Baly to investigate the action of ultra-violet light on carbonic acid adsorbed on surfaces. It was found that when

various insoluble substances capable of adsorbing carbonic acid were suspended in pure water through which a stream of carbon dioxide was passed, and the whole exposed to ultra-violet light, complex organic compounds were formed which could be recovered by evaporation of the solution after filtration. Among the powders which behaved in this way were aluminium metal, barium sulphate, freshly precipitated aluminium hydroxide, and the basic carbonates of aluminium, magnesium, and zinc.

It is interesting to note that when the precipitated and washed aluminium hydroxide was allowed to stand in water for 24 hours the preparation was markedly less effective, and that after standing for 60 hours no appreciable amount of organic matter was formed on irradiation in presence of carbonic acid. Besides being an excellent control experiment, this result lends significant support to the adsorption mechanism, since it is known that in contact with water aluminium hydroxide gradually becomes acidic in character and consequently no longer adsorbs carbonic acid. The filtrate from the irradiated suspension usually contains up to 0·03 grm. per litre (after 2 hours' exposure to a Hewittic vacuum burner at 6 inches) of organic matter. This material appears to consist of complex carbohydrates, since it chars readily, and although it gives no reduction with Benedict's solution, it nearly always develops reducing power after hydrolysis with hydrochloric acid. It may be stated that Baly and his collaborators took great pains to see that organic impurities did not enter into the experiments at any stage.

In the second paper Baly, Stephen and Hood [23] discuss the photosynthesis of carbohydrates from carbonic acid by means of visible light. In the first paper the surfaces considered were all white. Stephen now suggested the use of coloured materials with a view to effecting the photosynthesis by means of visible light. It was found that suspensions of nickel carbonate or cobalt carbonate in aqueous carbonic acid gave organic matter on exposure to visible light (*i.e.* ordinary half-watt lamps and glass

reaction vessels). The organic material reduced Benedict's solution, gave the Molisch and Rubner reactions, and formed a solid osazone. It also contained one or more complex substances which reduced Benedict's solution after acid hydrolysis. Under comparable conditions the use of visible light and coloured surfaces gave a larger yield of organic matter than the use of ultra-violet light and white surfaces, and, moreover, the carbohydrate content was higher. This simply means that the exclusion of ultra-violet light prevents the photo-decomposition of the carbohydrates synthesised. If a solution of ammonium carbonate containing a suspension of nickel or cobalt carbonate is exposed to visible light, complex nitrogenous organic compounds are formed. In the course of the work it was noticed that the catalytic surface gradually lost its activity, owing to the formation of a surface film of oxide. The oxygen is, of course, liberated in the photosynthetic process. It was found that in the presence of a badly poisoned surface intense visible light decomposed the carbohydrates formed during the first stages of the experiment when the surface was fresh. It must again be emphasised that Baly, Stephen and Hood carried out very careful control experiments, which seem to exclude the possibility that the carbohydrates were formed from impurities present in any of the reactants or reaction vessels.

In the third paper Baly and Davies [24] discuss the interpretation of the work under the title "Photosynthesis *in vivo* and *in vitro*." The authors point out that, although Willstätter has proved that the molecular ratio of carbon dioxide assimilated and oxygen transpired is unity in the leaf, no one has ever detected formaldehyde in the leaf. This fact is at any rate not inconsistent with the view that activated carbonic acid gives an unstable product which at once polymerises in the light to carbohydrate. The next step in the argument is the production of evidence that in the leaf photosynthesis occurs in the chloroplasts, and probably at the bounding surface of the lipoid and

aqueous phases. It is shown further that the thermochemical equation

$$6H_2CO_3 \rightarrow C_6H_{12}O_6+6O_2-673{,}800 \text{ calories}$$

demands that a minimum frequency of $1{\cdot}1754\times10^{15}$, corresponding with a wave-length of $255{\cdot}2\mu\mu$, is necessary for activation of carbonic acid by means of radiation alone. Now, since photosynthesis occurs in the plant with *visible* light, some additional or alternative mode of activation must clearly be found. Baly and Davies then argue that the experiments already detailed make it probable that photosynthesis is a photochemical reaction at a surface, and that the adsorbed carbonic acid is partially activated in the leaf in virtue of its adsorbed condition, and that visible light completes the activation. "In other words, the total quantity of energy necessary for photosynthesis to take place is supplied in two separate amounts, one quantity being given when the adsorption on the surface takes place, and the second quantity being given by light."

The peculiar merit of a coloured surface is explained as follows: if the surface gives up energy to carbonic acid, it must be reactivated before it can hand on energy to a fresh layer of adsorbant. Reactivation of the surface must be by ultra-violet light in the case of a white surface, since visible light is not absorbed, but in the case of a coloured surface such reactivation of the surface would probably be secured by visible light. The following features appear to be common to photosynthesis in the leaf and in the surface experiments: ordinary formaldehyde does not enter into the reactions, surfaces and visible light play an important part, and fatigue effects are observed in both cases. For both processes there is a slow recovery from fatigue, and synthesis cannot proceed more rapidly than the recovery reaction. It is further concluded that the yields *in vitro* and *in vivo* are not seriously at variance when compared in terms of grams formed per hour per sq. cm. The recovery process in the plant is probably concerned

with the equilibrium of the pigments: chlorophyll-A., chlorophyll-B., carotin, and xanthophyll.

In concluding this brief summary of the work of Baly and his collaborators it is impossible for one who has witnessed the progress of the investigations not to pay tribute to the skill, patience, and ingenuity which lie behind these results.

The writer has worked in Professor Baly's laboratory throughout the period over which the researches have extended, and as a spectator engaged in other directions has been able to realise the immense difficulties which have been overcome. It is not too much to say that we have now for the first time a consistent set of working hypotheses connecting the most fundamental chemical reactions known to science—the photochemical syntheses in the living plant—with laboratory chemistry. Phytosynthesis is the most efficient method of utilising the energy income of the earth in the form of solar radiation, and the successful elucidation of its mechanism may prove to be of great significance.

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The Action of Light on Organic Compounds.—It is evident that the response of an organic compound to light of different wave-lengths will depend in the first instance on the absorption spectrum of the substance concerned. Only those rays which are absorbed will have any chance of causing a chemical change, but it by no means follows that because light is absorbed chemical change must occur. Now the field of the absorption spectra of organic compounds has been intensely cultivated during the last quarter of a century, but the interpretation of the results has not yet reached a very advanced stage. We are not in general able to predict the absorption of a compound of a given structure, although argument from the nearest analogous compound has often proved correct. The position concerning the photochemistry of organic compounds is made even worse than that concerning the meaning of the absorption spectra by the fact, that given an absorption curve we are entirely unable to state beforehand whether there will or will not be observed a parallelism between the spectral distribution of efficiency for a photochemical change and the variation of intensity of absorption with wave-length.

It is possible to make certain generalisations which hold reasonably well. Drastic decomposition of organic molecules requires short-wave ultra-violet light, and it is safe to say that no very deep-seated changes occur with light on the long-wave side of 240–250$\mu\mu$. The shorter the wave-length beyond this point the more energetic the chemical changes. Both ozone and hydrogen peroxide can be synthesised under suitable conditions with extreme ultra-violet rays, and these compounds may enter into a variety of side reactions with either the reactants or the resultants in another photochemical change.

It will be seen that in many reactions, such as the photolysis of potassium nitrate and of acetone, that a very large percentage of the decomposition is due to the very short ultra-violet rays, although the near ultra-violet may be absorbed. Very intense ultra-violet radiation, which

includes the whole output of a new mercury vapour lamp, is capable of splitting many organic compounds so drastically that carbon dioxide, methane, hydrogen, and water are formed. The near ultra-violet and even visible rays either effect no chemical change when they are absorbed or else bring about a molecular rearrangement or a condensation or a polymerisation. Many reactions are catalysed by ultra-violet rays, although it is but very rarely that the photosynthesis proceeds in a simple manner. It is only necessary to consider the recent experience of workers in the polymerisation of formaldehyde (Baly and his collaborators, see p. 83) to realise how very complicated a photochemical reaction or set of reactions can be. The complications can only be avoided by the use of something approaching monochromatic light, but directly the use of filters becomes necessary to a photochemical reaction light must be regarded as a very expensive method for supplying the energy required.

In order to illustrate the general position with regard to the photochemistry of organic compounds a series of tables has been prepared, giving very briefly a few examples of the commonest types of changes, viz. photo-polymerisations, isomeric changes, photo-decompositions, and photosyntheses.

PHOTO-POLYMERISATION

Reaction.	Reference.
Acetylene $\xrightarrow{\text{u.v.}}$ solid yellow polymer (no benzene).	Berthelot and Gaudechon, *Compt. rend.*, 1910, **150**, 1169; Mathews and Dewey, *ibid.*, 1910, **151**, 395.
Ethylene→liquid polymer b.p. below 100° C., rancid odour.	
Cyanogen→para-cyanogen.	Berthelot and Gaudechon (*loc. cit.*).
Acrolein→solid in 90 minutes under radiation from mercury lamp.	Moureu, Dufraisse and Badoche, *Bull. Soc. chim.*, 1924, **35**, 1572, 1591.
Diphenylene-ethylene→insoluble form with 10 minutes' exposure to a quartz-mercury lamp.	Ferrier, *Chem. Abstracts*, 1923, **17**, 3177.
Vinyl esters form celluloid-like solids on irradiation.	Klatte and Tollett, U.S.P. 1241738, Oct. 2, 1917.

PHOTO-POLYMERISATION—*continued*

Reaction.	Reference.
Vinyl chloride → amorphous insoluble form, sp. gr. 1·406.	Baumann, *Annalen*, **163**, 317.
$CH_2:CHCl \rightarrow (CH_2:CHCl)_{16}$ under the influence of the extreme u.v. from a mercury lamp.	Plotnikow, *Z. wiss. Phot.*, 1922, **21**, 117.
Vinyl bromide → polymer insoluble in water, alcohol, ether, sp. gr. 2·075, decomposes at 125–130° C.	Baumann (*loc. cit.*).
Vinyl bromide → "caouprene bromide." (Wave-lengths longer than 330$\mu\mu$ (sunlight).)	Ostromuislenski, *J. Russ. Chem. Soc.*, 1912, **44**, 204.
p-Vinyl anisole ⇄ polymer. (Wave-lengths shorter than 330$\mu\mu$.)	Stobbe and Toepfer, *Ber.*, 1924, **57**, 484.
Long exposure to diffuse daylight. β-Ethyl mesityloxidoxalate → dimeric form	Federlin, *Annalen*, **356**, 261.
Anthracene ⇄ dianthracene. (see below)	Downes, U.S.P. 1,303,039 Luther and Weigert, *Sitz. K. Akad. Wiss.*, Berlin, 1904, 828.
Indene resinifies (polymerisation) under u.v. light.	Stobbe and Farber, *Ber.*, 1924, **57**, 1845.
Stilbene in benzene solution is largely polymerised by u.v. light.	Stobbe, *Ber.*, 1914, **47**, 2701.
Drying oils undergo on exposure to daylight slow polymerisation, accelerated by u.v. light.	Marcusson, *Z. angew. Chem.*, 1922, **35**, 543.

Some of the above changes may now be considered in more detail. Luther and Weigert (*loc. cit.*) found that when a boiling solution of anthracene in phenetole, anisole, or xylene is exposed to the light from an arc lamp, considerable quanitites of dianthracene (m.p. 270–280°) are formed. If, however, a suspension of dianthracene in boiling phenetole is kept in the dark for 20 hours the reverse reaction occurs, and the whole of the insoluble dimeride is converted into soluble anthracene. The depolymerisation follows the law for a unimolecular reaction. The whole sequence of changes is expressed clearly by the equation:

$$\underset{\text{(soluble in boiling phenetole)}}{\text{Anthracene}} \underset{\text{dark}}{\overset{\text{u.v. light}}{\rightleftharpoons}} \underset{\text{(insoluble in boiling phenetole)}}{\text{Dianthracene}}$$

Downes made use of the photo-polymerisation as follows : crude anthracene is dissolved in coal-tar naphtha, benzene, or toluene and the solution is irradiated. Dianthracene is slowly precipitated, whilst impurities such as carbazole and phenanthrene remain in solution. The polymeride may be separated by filtration and converted into anthracene by sublimation. The product is fairly pure.

The photo-polymerisation of vinyl esters appears to hold out industrial possibilities. Klatte and Tollett state that the change may be catalysed by using benzoyl peroxide, ozonides, and anhydrides of organic acids in conjunction with oxygen-yielding materials such as percarbonates, perborates, and silver oxide. The products are colourless, transparent, odourless solids, which can be turned, cut, or planed. They become plastic in hot water and harden again on cooling. Kuhl states that vinyl acetate and chloracetate polymerise under ultra-violet rays to give fireproof substitutes for celluloid. As an illustration of the method of preparation, using both light and heat to assist the reaction, the following may be given : 1 kilogram of vinyl chloracetate is mixed with 0·5–1·0 gram of benzoyl peroxide and carefully heated in a large vessel provided with a reflux condenser. Polymerisation proceeds rapidly with evolution of heat as soon as the temperature exceeds 100°. At this stage the reaction vessel should be strongly cooled, and the addition of an inert solvent such as chlorobenzene (300 grams) is desirable. A thick syrup is thus formed, which is then converted into a solid mass under the action of ultra-violet light. In solution this product acts as a good lacquer. The polymerisation of vinyl chloride in 2½ per cent. methyl alcoholic solution yields something resembling a synthetic rubber.

PHOTOCHEMICAL DECOMPOSITIONS

Substance.	Products.	Reference.
ACETALDEHYDE, with rays longer than $300\mu\mu$,	Carbon monoxide and methane.	Berthelot and Gaudechon, *Compt. rend.*, 1913, **156,** 233.
with rays shorter than $250\mu\mu$ polymers are formed rapidly,	Meta- and para-acetaldehyde.	
with near and extreme u.v. and in the presence of oxygen and water.	Acetic and formic acids are formed most readily if the aldehyde is in the vapour state.	
ETHYL ALCOHOL ..	Acetaldehyde and hydrogen (some carbon monoxide and ethane).	Ditto, *Jour. Soc. Chem. Ind.*, 1911, **30,** 1086.
ACETIC ACID (in absence of air).	Combustible gases 39%; carbon dioxide 44%; carbon monoxide 17%.	*Ibid.*, 1910, **29,** 1081.
ACETONE	Carbon monoxide 49 vols.; ethane 46 vols.; methane 5 vols.;	Ditto, *Compt. rend.*, 1910, **151,** 478.
	with sunlight methane and acetic acid are formed.	*Ibid.*, **150,** 1164.
in aqueous solution	Exposure to monochromatic rays causes the formation of acid.	Henri and Wurmser, *ibid.*, **155,** 503.
GLYCEROL (10% solution in water)	Formaldehyde, acids, etc. (the addition of hydrogen peroxide facilitates the decomposition).	Henri and Ranc, *Compt. rend.*, 1912, **154,** 1261.
GLYCEROL-WATER SYSTEM	Glycerose, glyceric aldehyde.	Bierry, Henri and Ranc, *Compt. rend.*, 1911, **152,** 535.
(alkaline)	β-Acrose.	
LACTIC ACID ..	Some acetic acid, no methane or alcohol.	Baudisch, *Biochem. Z.*, 1920, **103,** 59.
CALCIUM LACTATE (solid)	Carbon monoxide, methane, ethane, hydrogen.	Berthelot and Gaudechon, *Compt. rend.*, 1910, **151,** 478.
OXALIC ACID ..	Carbon dioxide and formic acid $H.COOH \rightarrow CO + H_2O$	*Compt. rend.*, **158,** 1791.
	Glyoxylic acid, carbon monoxide, carbon dioxide, water.	Bauer, *Z. Physikal. Chem.*, 1924, **111,** 315.
Ditto sensitised, see page 62.	.. .. ..	*loc. cit.*
UREA, and also amines, amides, acetonitrile, etc. (u.v. rays).	Ammonia and then ammonium nitrite.	*Compt. rend.*, 1911, **152,** 522.
Formamide (u.v. rays)	Dehydrates with formation of hydrocyanic acid.	*Ibid.*, 1910, **150,** 1164.
ETHYL ACETOACETATE, ACETYLACETONE.	Ethyl acetate and acetic acid, acetone and acetic acid.	Grossman, *Z. Physikal. Chem.*, 1924, **109,** 305.

PHOTOCHEMICAL DECOMPOSITIONS—*continued*

Substance.	Products.	Reference.
DIACETYL VAPOUR in water.	Ethane and carbon monoxide, acetic acid, and acetaldehyde.	Porter, Ramsperger and Steel, *Jour. Am. Chem. Soc.*, 1923, **45**, 1827.
SUGARS—Sucrose ..	(1) Inversion; (2) glucose and fructose are decomposed, giving alcohols, aldehydes, and ketones; (3) finally with prolonged irradiation carbon monoxide, carbon dioxide, and hydrogen are formed.	Berthelot and Gaudechon, *Compt. rend.*, 1912, **155**, 1153.
Glucose and fructose	Glucose or fructose subjected separately to u.v. rays gives the same products.	Bierry, Henri and Ranc, *Compt. rend.*, 1911, **152**, 1629.
	Extreme u.v. rays are the most effective.	Beyersdorfer and Hess, *Ber.*, 1924, **57B**, 1708.
	Condensation products, like caramel and dextrin, may also occur, *e.g.* on the surface of sucrose crystals exposed to u.v. at 70° C.	
Maltose	Behaves qualitatively the same as fructose and and glucose.	
Fructose in water	CO, CO_2, formaldehyde, and methyl alcohol.	Bierry, Henri and Ranc, *Compt. rend.*, 1910, **151**, 316; Bierry and Ranc, *Bull. Soc. Chim.*, 1924, **35**, 771.
STARCH in water solution	Hydrolysis and partial oxidation occurs with formation of dextrins, maltose or reducing sugars, pentoses, formaldehyde.	Bielecki and Wurmser, *Compt. rend.*, 1912, **154**, 1429; Massol, *ibid.*, 1911, **152**, 902.
CELLULOSE	Oxycellulose is formed after long exposure to a mercury lamp—tensile strength is lost.	Dorée and Dyer, *J. Soc. Dyers and Col.*, 1917, **33**, 17.
CARBON DISULPHIDE	Sulphur is liberated and there is a tendency to form yellow resinous substances.	Bruhat and Pauthenier, *Compt. rend.*, 1924, **178**, 1536.
MONOCHLORACETIC ACID, MONOBROMACETIC ACID	Hydrolysis occurs, liberation of halogen. (Monochromatic light, 254 $\mu\mu$.)	Rudberg, *Z. Physik.*, 1924, **24**, 247.
cis- and trans-$\alpha\beta$-DI-IODOETHYLENE $\alpha\alpha$-DIIO	Iodine liberated.	Kaufmann, *Ber.*, 1922, **55**, 249.

PHOTOCHEMICAL DECOMPOSITIONS—*continued*

Substance.	Products.	Reference.
ALKYL HALIDES ..	Halogens liberated (*vide infra*).	Stobbe and Schmitt, *Z. wiss. Phot.*, 1920, **20**, 57.
TOLUENE	A small quantity is decomposed with formation of benzaldehyde, benzoic acid, and formic acid. Hydrocarbons and condensation products of benzaldehyde also appear to be formed.	Kailan, *Monatsh.*, 1920, **40**, 445.

The following substances will be discussed: glycerol, acetone, acetaldehyde, oxalic acid, sugars, starch, and cellulose.

Glycerol.—The effect of quartz-mercury lamp radiation on glycerol-water mixtures has been studied by Bierry, Henri and Ranc (*loc. cit.*). Neutral glycerol at 25° in the presence of air reacts to form a glycerose, giving a positive phloroglucinol reaction for glyceric aldehyde, although the "yield" is very small.

In the presence of alkali, β-acrose, identified by its phenylosazone, was formed in small amount. Salts of uranium, and to a lesser extent iron and cobalt, appear to assist the photochemical decomposition of glycerol. In a later investigation Henri and Ranc (*loc. cit.*) found that a 10 per cent. aqueous solution of glycerol gave formaldehyde and other acidic and aldehydic bodies. The addition of hydrogen peroxide considerably facilitated the decomposition of glycerol.

Acetone.—The work of Henri and Wurmser on acetone is of interest, owing to the simplicity of the results. The rate of formation of acid under the action of monochromatic rays in the region 214·4–298·1$\mu\mu$ shows an interesting parallelism between the chemical effects and the absorption curve. It is somewhat unusual to find, as in this case, that

the very short ultra-violet wave-lengths are less effective than the near ultra-violet rays.

Acetaldehyde.—The investigations of Berthelot and Gaudechon on acetaldehyde afford an excellent idea of the complexities which have to be faced in the analysis of the photochemistry of quite simple substances. In the absence of oxygen near ultra-violet rays cause little decomposition, whilst with shorter wave-lengths some acetic acid is formed. Reaction occurs more quickly in the vapour than in the liquid state. It is also possible for polymerisation to occur if rays shorter than $250\mu\mu$ are used, both para- and meta-acetaldehyde being formed. Resinification may also take place to some extent under the action of the extreme ultra-violet rays. Now, if water is present the tendency towards polymerisation is greatly weakened, and acetic and formic acids are produced with some readiness. If acetaldehyde is exposed to quartz-mercury radiation which has been subjected to the screening action of a glass plate so that no rays shorter than $300\mu\mu$ are transmitted the decomposition will very largely follow the course indicated by the equation :

$$CH_3CHO \rightarrow CO + CH_4$$

but small quantities of ethane are also formed. Ethyl alcohol is slowly decomposed by short-wave ultra-violet radiation with the production in the first instance of acetaldehyde and hydrogen.

Sugars.—The photochemical decomposition of sucrose may be followed by measurements of optical rotation, acidity, or reducing power, and by collecting the gaseous products formed. Euler and Ohlsen observed that hydrolysis occurred under a mercury vapour lamp at a rate greatly exceeding that which could be ascribed to the heating effect. Acid was formed in small amounts, and the rate of hydrolysis varied with the changes in hydrogen ion concentration, *i.e.* increased with increasing acidity. Bierry, Henri and Ranc varied the conditions by carrying out tests with 5 per cent. solutions of calcium hydroxide *in vacuo*, in air, and with the addition of calcium

carbonate. Appreciable hydrolysis occurred in one day when the solution was maintained at 40° *in vacuo*, whilst in two days it was possible to detect formaldehyde in the solution. After three days evolution of gas began to occur, and further irradiation resulted in the liberation of carbon monoxide, carbon dioxide, and hydrogen. Beyersdorfer and Hess found that the first effect was inversion, and that the reaction was very slow at 20°, but much more rapid at higher temperatures. After inversion the mixture of fructose and glucose gave organic acids, ketones, alcohols, aldehydes, and methane in addition to the gases already mentioned. Condensation products, dextrin, and "caramel" were also formed. Berthelot and Gaudechon analysed the gaseous products formed from 10 per cent. aqueous solutions of sugars with the following result:

Sugar.	Combustible gases (100). CO	CH_4	H_2	Carbon dioxide.
Sucrose	45	8	47	16
Glucose	12	12	76	22
Maltose	12	11	77	21
Fructose	83	8	9	15

It will be seen that the photochemical degradation follows the same qualitative lines for different sugars, but that quantitatively the results may be quite different. Even when glucose and fructose are examined separately the reactions differ quantitatively.

Berthelot and Gaudechon state that the order of increasing resistance to photochemical decomposition is as follows: ketoses, aldoses, straight-chain polyhydric alcohols, ringed polyhydric alcohols. Whilst the ketoses are affected by ultra-violet rays longer than $300\mu\mu$ (*i.e.* by sunlight), aldoses, dextrose, mannose, and galactose require rays in the region 250–$300\mu\mu$, and the alcohols are only changed under the action of waves shorter than $250\mu\mu$. In most cases the first change results in the formation of an alcohol corresponding with the sugar but containing one atom of carbon less in the molecule, whilst carbon monoxide and hydrogen are set free. As a result of secondary reactions carbon dioxide and methane are

formed, and the resulting acid solution reduces ammoniacal silver nitrate and Fehling's solution. Beyersdorfer and Hess (*loc. cit.*) examined the effect of adding green colouring-matters such as chlorophyll and Badische green PLX to aqueous solutions of sucrose and observed practically no decomposition. Sodium acetate also exerted an inhibitory effect, but manganese chloride and the potassium halides had little or no influence on the course of the reaction. Berthelot and Gaudechon found that the decomposition of fructose could be used as an ultra-violet actinometer, the volume of gas liberated by 10 per cent. aqueous solutions being proportional to the time. For weak solutions the reaction velocity varied as the concentration, but for very strong solutions a constant rate was observed, indicating that the velocity depended on the absorptive power of the solution. Bierry and Ranc, however, observed that the decomposition was more drastic, since they recognised carbon monoxide, carbon dioxide, and formaldehyde among the products.

As will be seen from the treatment of Baly's work given separately (see p. 83), formaldehyde undergoes photochemical condensation or polymerisation with the formation of sugars, acids, and other products. It needs little imagination to visualise the complex nature of the reactions involved when we see that photochemical degradations and syntheses can occur in the reacting system.

Starch and Cellulose.—Bielecki and Henri have subjected aqueous solutions of pure starch to the action of ultra-violet rays. Hydrolysis followed by oxidation occurs, and formaldehyde, reducing sugars, pentoses, and dextrin have been recognised among the products of decomposition. Massol had observed earlier that soluble starch gradually lost the power of giving the blue iodide complex. In the presence of sulphuric acid the solution acquires reducing power on irradiation and maltose is probably formed. Experiments on the action of light on cellulose have shown that oxycellulose is formed with complete loss of tensile strength.

PHOTOCHEMICAL SYNTHESIS

Reactants.	Resultants.	References.
Hydrogen peroxide, ozone, formaldehyde, sugars.	*See* separate sections.	
Acetic acid and aniline (equimolecular proportions).	Theoretical yield of acetanilide with 24 hours' u.v. irradiation.	Stoermer and Robert, *Ber.*, 1922, **55B**, 1030.
Propionic acid and aniline.	Propionanilide in 65% yield.	
Benzoic acid and aniline.	Benzanilide in small yield.	
Ammonium acetate and ammonium hydroxide in excess.	Acetamide in 5% yield.	
Benzaldehyde and oxygen at the temperature of solid carbon dioxide.	U.v. light favours the formation of considerable quantities of a peroxide body, in addition to the usual benzoic acid.	Suida, *Ber.*, 1914, **47**, 471.
Benzaldehyde (1 mole), acetic anhydride (3 moles), oxygen atmosphere.	Benzoyl acetyl peroxide favoured by light from arc.	Jorissen and Ringer, *Centr.*, 1905, **76**, i., 817.
Aldehydes, oxygen, or oxygen-containing gases at low temps.	Per-acids.	B.P. 16849, July 22, 1913.
Ketones and anhydrous alcohols exposed to quartz-mercury vapour lamp.	Pinacols.	*J.C.S. Abstr.*, 1915, **108**, ii.
Iso-eugenol and air u.v. rays.	Vanillin.	Wood, *Chem. and Met. Eng.*, 1923, **28**, 399.
Eugenol and air u.v. rays (temperature, 50–60° C.).	Vanillin (95% yield).	Genthe and Co., D.R.P. 224071.
Methyl alcohol and potassium nitrite (diffuse daylight or u.v. rays).	Potassium formhydroxamate.	Baudisch, *Ber.*, 1911, **44**, 1009; 1916, **49**, 1176; 1918, **51**, 193.
Formaldehyde and nitrite.	Potassium formhydroxamate.	Baly, Heilbron and Hudson, *J.C.S.*, 1922, **121**, 1078; *J.S.C.I.*, 1922, **41**, 609.
Formhydroxamic acid and glycine, "activated" formaldehyde.	α-Amino acids, pyrrole, pyridine, alkaloidal substances.	Ditto.
Ammonia and carbon dioxide-water.	Methylamine, nitrous and nitric acids, pyridine.	Baly, Heilbron and Stern, *J.C.S.*, 1923, **123**, 185.

In the field of photochemical synthesis few reactions proceed quantitatively. Acetic acid and aniline react to give 100 per cent. yields of acetanilide after 24 hours' irradiation with a quartz-mercury lamp. The formation of propionanilide only occurs in 65 per cent. yield, and in the case of benzanilide the yield is even worse. Amides are not at all readily formed, since even in the favourable case of acetamide the yield on irradiating ammonium acetate in the presence of excess of ammonium hydroxide does not exceed 5·3 per cent.

A process with considerable possibilities has been proposed for the formation of vanillin. By passing a current of air through iso-eugenol subjected to powerful ultra-violet radiation vanillin is readily formed. The mechanism of the reaction may be related to the formation of ozone under the action of the light. Unfortunately the iso-eugenol darkens rapidly, and the consequent loss in transmission very much hinders the process. It is therefore imperative to have the original liquid in a highly clear state, a condition which requires the use of redistilled iso-eugenol. The circulation of large quantities of air also involves considerable losses, as the iso-eugenol is carried away as a result of its not inconsiderable vapour pressure. A German patent proposes the oxidation of eugenol maintained at 50–60°. A current of air is passed through the irradiated solution and the yield of vanillin is 95 per cent.

An interesting field in photosynthesis has been opened up by the work of Baudisch, and Baly, Heilbron and Hudson, on formhydroxamic acid. According to the former investigator, methyl alcohol reacts with potassium nitrite in the presence of diffused daylight or ultra-violet light with the formation of potassium formhydroxamate CHOH:NOK. The latter investigators found that formaldehyde and nitrites reacted (*a*) in ultra-violet light, and (*b*) in visible light in the presence of a catalyst to give the reactions :

$$\text{H.CHO} \xrightarrow{\text{light}} \text{H.C.OH (activated formaldehyde)}$$

$$\text{H.C.OH} + \text{O:N.OK} \rightarrow \begin{matrix}\text{H.COH}\\ \| \\ \text{O:N.OK}\end{matrix} + \begin{matrix}\text{H.COH}\\ \| \\ \text{N.OK}\end{matrix} + \text{O}$$

Secondary reactions also occur, and glycine as well as other amino acids have been isolated. Pyridine and piperidine and certain alkaloids have also been detected in investigations of this type.

PHOTOCHEMICAL REARRANGEMENTS

Reaction.	References.
o-Nitrobenzaldehyde → *o*-Nitrosobenzoic acid.	Weigert and Kummerer, *Ber.*, 1913, **46**, 1207.
Cinnamylidenemalonic acid → Diphenyltetramethylenediethyldicarboxylic acid.	Hartley and Scott, *J.C.S.*, 1924, **125**, 1233.
Fumaric acid → Maleic acid.	Kailan, *Z. Physikal. Chem.*, 1914, **87**, 333.
Crotonic acid → Isocrotonic acid.	Stoermer and Robert, *Ber.*, 1922, **55B**, 1030.
The methyl ester of benzoyl acrylic acid is yellow and is changed by sunlight into the colourless stereoisomeride.	Rice, *Am. Soc.*, 1923, **45**, 222; 1924, **46**, 214, 2319.
Cinnamic acids, either molten or in solution, undergo isomeric change on irradiation with wave-lengths, including the range 270 and 320$\mu\mu$.	Stobbe, *Ber.*, 1919, **52**, 666; Stobbe and Steinberger, *Ber.*, 1922, **55B**, 666.
Coumaric acids undergo stereoisomeric change, stable form $\xrightarrow[\text{u.v.}]{}$ labile form.	Stoermer, *Ber.*, 1909, **42**, 4865; 1911, **44**, 637.
N-chloroacetanilide undergoes isomeric change in u.v. light $CH_3CONClC_6H_5 \rightarrow CH_3CONHC_6H_4Cl$.	Blanksma, *J.C.S.*, 1902, **82**, 646. Chattaway and Orton, *ibid.*, **81**, 200; Mathews and Williamson, *Am. Soc.*, 1923, **45**, 2574.
Benzoylphenylethylene oxide; Benzoyl-*m*-nitrophenylethylene oxide; Benzoyl-*p*-chlorophenylethylene oxide; all undergo rearrangements so that phenyl α-hydroxystyryl ketones are formed when the solutions in methyl alcohol are subjected to u.v. rays (yields are small).	Bodforss, *Ber.*, 1918, **51**, 214.
3-Phenyl-2-methylindone undergoes complex rearrangements.	De Fazi, *Chem. Abstr.*, 1924, **18**, 2173.
Some semicarbazones yield stereoisomerides under the action of u.v. radiation.	Wilson and Macaulay, *J.C.S.*, 1924, **125**, 841.
Anti-aldoximes $\xrightarrow[\text{u.v.}]{}$ *syn*-isomerides.	Ciamician and Silber, *Ber.*, 1903, **36**, 4268; Brady and McHugh, *J.C.S.*, 1924, **125**, 547.

The photochemical transformation:

o-Nitrobenzaldehyde → *o*-Nitrobenzoic acid

is a simple case of isomeric change. The reaction has

been studied quantitatively in a neutral solvent, using monochromatic light. This is one of the few reactions which conform to the Einstein Law of Photochemical Equivalence, and, indeed, it forms one of the best arguments for the validity of that generalisation.

A good deal of information is available on the effect of light in inducing photochemical rearrangement; but as the work has as yet little practical utility, the bald summary given in the table must suffice.

Fading of Dyestuffs.—The fading of dyestuffs is of enormous industrial significance, and as the process is usually very slow it has become a matter of importance to have a quick method for determining the fastness. Ultra-violet radiation has proved a very useful agency for accelerating the ageing phenomena.

Let us first enumerate the variables:

(*a*) Fabrics: cotton, silk, wool, linen, rayon, etc.

(*b*) Dyestuffs: a tremendous range of colouring matters of widely differing chemical character is available.

(*c*) Weather and environment: the dyed fabric when put out to service is subjected to sunlight, electric light, and an atmosphere varying in humidity and in the extent to which it is polluted.

(*d*) Quick ageing methods involve the use of light sources having different spectral energy distributions from sunlight, and emitting wave-lengths absent from daylight or ordinary artificial light. The special light sources, moreover, differ amongst themselves.

It would be easy to make out an apparently strong case against any method of accelerating the fading of dyed fabrics, but before considering possible objections it will be well to consider an ordinary fading test. Sunlight and rain are very variable factors, and without laborious and (possibly untrustworthy) methods of control, an open-air test is at best only very approximate. In order to carry out a test with the dry fabric it must be enclosed under quartz, as glass does not transmit the near ultra-violet rays of sunlight.

The quartz-mercury lamp has the advantage of great intensity and consequently a rapid fading action, but, on the other hand, it may be responsible for the photochemical formation of ozone and hydrogen peroxide, either of which may act on the dyestuff by chemical as distinct from photochemical methods.

The well-known deterioration of mercury vapour lamps involves the difficulty that the mere statement "x hours' quartz-mercury irradiation at a distance y" has no meaning even with lamps of the same make. Actinometric control is desirable if reproducible results are to be obtained. In view of these considerations it is not surprising that other light sources have been tried. Gordon [1] prefers the violet carbon arc, and Mott and Bedford [2] the flame-arc in conjunction with a crown-glass filter. Pierce [4] strongly favours the mercury lamp. Under the conditions described in his paper one hour's exposure was equivalent to about eight hours of sunshine. Certain American Government departments stipulate 48 hours as a suitable exposure under these conditions, but few dyes are fast under this somewhat drastic test. Scheurer [5] found that it was necessary to protect the dyes against the ozone formed by the lamp. He found that certain dyes which were stable in sunlight were affected in 24 hours by the mercury lamp, although indigo faded more rapidly in sunlight than under the arc. Gebhard [6] considers that the bleaching action of light is due in the first instance to the formation of peroxides of the dyestuffs, rather than hydrogen peroxide. It has been shown by Harrison [7] that in the presence of air cellulose is decomposed by the light from the quartz lamp with formation of reducing substances. In a vacuum, cellulose acquires no reducing power under the action of sunlight, thus perhaps explaining why direct colours do not fade under these conditions. Flynn regards the fading of direct dyes as a reduction process which is accelerated by the action of ultra-violet radiation on cellulose.

Basic dyes probably fade as a result of oxidation processes. The formation of reducing compounds occurs more readily with cotton than with silk and wool.

It would seem to the writer that the following arrangement offers a good chance of providing a reasonable means for relatively quick and reproducible testings, offering a fair approximation to natural conditions.

The dyed fabric is enclosed in a shallow, gas-tight box, with a lid fitted with panes of the proprietary *vitaglass*. The humidity of the chamber may be regulated by passing air through suitable saturators or drying trains. A quartz-mercury lamp is placed at a definite distance from the box, and its output controlled by one of the actinometric reactions discussed (see p. 50). The test would approximate to a rapid sunlight test under constant conditions.

There can be no doubt from the literature that a wide field of usefulness is open to accelerated fading tests, but one is impressed with the necessity for a careful perusal of the original memoirs and for the avoidance of hastily drawn conclusions.

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INK TESTING

1. Rupert, *Ind. Eng. Chem.*, 1923, **15**, 489.
2. U.S. Bureau of Standards Circular, No. 95, 28th June, 1920.

Rubber.—The vulcanisation of rubber may be hastened by the use of ultra-violet rays. Bernstein [1] exposed a benzene solution (rubber 6 per cent., sulphur 0·6 per cent.) and found that a moving film 0·5 mm. thick could be vulcanised with an exposure of 40–50 seconds. Xylene solutions of rubber and sulphur have also been used. Helbronner [2] found that after vulcanisation by means of

ultra-violet light the dried product was no longer soluble in the original solvent.

A phenomenon well known to users of mercury lamps in chemical laboratories is the deterioration of rubber tubing exposed to the light. This is due, according to Henri, to a kind of "after-vulcanisation." Schopper [3] tried the use of a dilute solution of dimethylaminomethylcoumarin to absorb ultra-violet rays, and thus protect balloon fabric from the deleterious action of sunlight. There seems to be no special reason for using this particular compound. Jakowsky [4] points out that the prevalent view that black rubber withstands light better than other varieties may possibly be explained by the opacity of the carbon black used. Asano [5] observed that as a result of the action of light on rubber in an inert atmosphere the material becomes insoluble in the usual rubber solvents. Both polymerising and depolymerising actions occur.

Wave-lengths shorter than $225\mu\mu$ apparently effect the former change, whilst longer wave-lengths depolymerise the rubber, the products suffering oxidation as a secondary reaction. The principal effect of sunlight is depolymerisation followed by accelerated oxidation. In order to protect rubber completely all rays shorter than $500\mu\mu$ must be excluded. As would be expected, ultra-violet irradiation has been tried for accelerated weathering tests, but in this case, as in the rapid examination of dyes for fastness, caution must be shown in interpreting the results.

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Cf. also "Weathering of Vulcanised Rubber," *J. Ind. Eng. Chem.*, 1926, **18**, 615.

Lithopone.—The well-known white pigment lithopone darkens on exposure to light. Roches (*Rev. Chim. Ind.*, 1922, **31**, 109) regarded the blackening as due to impurities.

The presence of iron, cobalt, cadmium, manganese, or radium did not cause blackening, but as little as 0·002 per cent. of chlorine destroyed the stability of lithopone exposed to ultra-violet light. Maas and Kempf [1] consider the darkening to be due to the zinc sulphide present in the pigment. The reaction:

$$2ZnS \rightarrow ZnS_2 + Zn$$

is assumed to occur by a photoelectric mechanism.

The light causes the transference of electrons from negatively charged S'' ions on the surface of the zinc sulphide crystal to positively charged zinc ions $Zn^{\cdot\cdot}$, so that uncharged atoms are formed. The zinc remains as free metal, whereas the sulphur combines to form zinc disulphide. It is said that "amorphous" zinc sulphide is not light sensitive. The reaction is not reversible in the dark, although the blackening may decrease owing to oxidation of the free metal.

Nishizawa [2] also held the view that coloration was due to the sulphide. He observed that mixtures of zinc sulphide and glycerol or other polyhydric alcohols did not darken on paper when exposed to ultra-violet rays. Rochelle salt and zinc tartrate exerted a similar effect in inhibiting the darkening. Magnesium and calcium hydroxides also acted as protecting agents, whilst linseed oil and turpentine did not interfere. These results are utilised in Brit. Pat. 156971 (Nov. 25, 1919), which covers a new method for the manufacture of lithopone.

Small amounts of glycerol, sugars, etc., salts and esters of tartaric acid, polyhydroxystearic acids are incorporated with the zinc sulphide. The organic compound itself or an aqueous solution may be used, and the sulphide may be precipitated in the presence of the compound, or else the organic compound may be formed in the presence of the sulphide. The sulphide thus formed withstands several hours' irradiation and also temperatures of 120° without darkening.

These results are not, however, in complete agreement

with the work of Job and Emschwiller.[3] These authors conclude that all varieties of zinc sulphide which darken under light must (*a*) contain some water ; (*b*) contain small amounts of metals or metalloids as impurities ; and (*c*) must have been heated.

The formation of zinc was observed in aqueous suspensions of zinc sulphide subjected in quartz vessels to the action of quartz-mercury radiation. Among the other products formed were hydrogen, hydrogen sulphide, and a zinc salt of a thionic acid. The presence of halogens has also been shown to favour the blackening process (Schleede, Herter and Kordatzki [4]).

The fact that darkening will not occur unless the sulphide has been ignited has also been confirmed by these authors.

Pfund [5] spread a thin layer of a cream of lithopone in water on to a quartz plate. This was then placed in the plate holder of a quartz spectrograph and exposed to the spectrum of the iron arc. The lithopone acted similarly to the photographic emulsion, since the darkest portions of the plate indicated the regions of maximum sensitivity. Wave-lengths longer than 320$\mu\mu$ caused little or no effect.

Research on the lines described have brought about a marked improvement in the light-resisting properties of lithopone. An old process lithopone showed a coloration under certain conditions in 4 seconds, whereas new process lithopones show no sign for periods varying from 35 to 135 seconds.

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Oils.—Ellis [1] found that the fluorescence of petroleum oils could be destroyed by ultra-violet irradiation. Other effects such as a change in colour were noted, some oils darkening and others undergoing partial bleaching. Oils possessing "gumming" properties tending to reduce their

efficiency as lubricants could be improved by irradiati(because certain unsaturated bodies became polymerized.

Claims have been made for (*a*) [2] application of ultr: violet light to the cracking of petroleum oils ; and (*b*) [3] cor version of hydrocarbons to acids and esters by means c ultra-violet rays and an air current. The German produc " voltol," [4] a good lubricating oil, is made by the action o: the silent electrical discharge on thin oils. The very short-wave radiation presumably effects either a polymerisation, or else the hydrogen which may be used in the process is " activated " so as to combine with the unsaturated constituents of the thin oils. " Voltol " is comparatively fluid at low temperatures and very viscous at high temperatures.

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4. *Engineering Progress*, 1922, 121.

An interesting patent has recently been taken out by Wright.[1] Paper is impregnated with gelatin, casein, or a similar protein substance and a solution of potassium or sodium bichromate. Exposure to the light from a quartz lamp results in both waterproofing and strengthening of the paper.

In their very useful book, *The Chemical Action of Ultra-Violet Rays*, Ellis and Wells give references to proposals to utilise the light in drying patent leather, testing paints, bleaching of oils and flour, and in certain analytical processes.

REFERENCE

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FILTERS USED FOR OBTAINING APPROXIMATELY MONOCHROMATIC LIGHT

For many purposes it is necessary to have available a source of light which is approximately monochromatic, *e.g.* pure red or pure yellow at a definite dominant wave-length.

Certain light sources are themselves roughly monochromatic without further precautions being taken, *e.g.* the light from a Bunsen burner into which a sodium salt is fed, since the D_1D_2 doublet preponderates over all other light-emission. Strictly monochromatic light is difficult to obtain with any great intensity, because the incident light must be dispersed by a prism or grating spectroscope. Only a relatively fine beam is allowed to pass through the slit of the spectroscope, and by the time the incident ray has suffered dispersion the intensity of light at a single frequency is never very great.

The desiderata for a satisfactory light as the source of monochromatic radiation are : (1) it must be available in very high intensity ; (2) its spectrum must show a few very strong lines rather than a closely packed arrangement of lines of moderate intensity ; (3) it must be available continuously over relatively long periods without great fluctuations in intensity. The light source which corresponds most clearly to these conditions is undoubtedly the quartz-mercury vapour lamp either of the "vacuum" or the "atmospheric" type.

If, however, a considerably less rigorous resolution is required the intense electric lamp of the "pointolite" type presents certain advantages. The spectrum is, of course, bounded by the limits of transmission of glass, but within these limits an even, continuous distribution of light is given. With suitable filters this lamp is very flexible in the range of monochromatism which can be obtained. It is possible, for instance, by this means to isolate strips of the spectrum some 50–100° Å.U. wide in regions between two strong lines in the spectrum of the mercury arc.

In the choice of light sources and filters the decision will rest always on the degree of monochromatism required and the selectivity of the filter, and it is frequently a nice point as to whether intensity or strict monochromatism can best be sacrificed.

Light filters may consist of dyed gelatin films, coloured glasses, or solutions. Excellent dyed gelatin filters are prepared by Messrs. Kodak and other manufacturers of

photographic materials (Wratten Light Filters, 1922; mercury monochromats, *cf.* Miethe and Stengel, *Z. Wiss. Phot.*, 1919, **19**, 57). The physical characteristics of the special gelatin filters are usually accurately specified. The transmission curves of a set of mercury monochromats are shown in Fig. 18.

For trustworthy laboratory controls liquid filters have much to recommend them. A selection of receipts is appended.

Barnard recommends Kettnow's solution. A saturated solution of copper nitrate mixed with chromic acid solution serves to eliminate the red and blue-violet regions. By

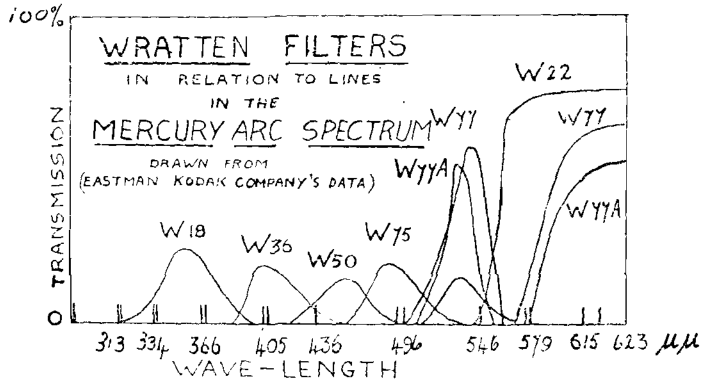

FIG. 18.

suitable variation of the proportions a greater or less degree of absorption at either end of the visible spectrum may be obtained. A solution containing 1 gram of crystallised copper sulphate, 75 c.c. of 0·880 ammonia, and 225 c.c. of water transmits in the region 405–436$\mu\mu$ (blue light). The mercury green line at 546$\mu\mu$ is transmitted selectively by the following solution: picric acid 0·4 gram, copper sulphate crystals 3·5 grams, didymium nitrate 15 grams, water 300 c.c. Picric acid solutions absorb strongly in the region 470–350$\mu\mu$. An excellent filter for transmitting the region 575–580$\mu\mu$ is made by dissolving 15 grams of potassium bichromate, 3·5 grams of crystalline copper sulphate, 1 c.c. of concentrated sulphuric acid in 300 c.c. of water.

Quartz lenses coated with silver precipitated from an alkaline silver solution by means of a 10 per cent. solution of milk sugar cut off practically the whole of the visible spectrum, but allow ultra-violet rays to be transmitted (Michaud and Tristan, *Sci. Amer.*, 1912, **107**, 257).

Cells made of cobalt blue glass and filled with a dilute solution of potassium bichromate transmit selectively in the infra-red.

R. W. Wood (*Phil. Mag.*, 1903, vi., **5**, 257) found that nitrosodimethylaniline absorbs rays in the region 390–500$\mu\mu$, but transmits those between 200 and 390$\mu\mu$. This substance makes an excellent filter for obtaining ultra-violet light, and it can be used either in solution or in the form of stained gelatin films.

A valuable and authoritative discussion of light filters has been given by Potapenko (*Brit. J. Photography*, 1921, **68**, 507).

ULTRA-VIOLET RAYS AND HALOGENATION

With the exception of fluorine, all the halogens are sensitive to light. The fluoride is the only silver halide unaffected by light. Calcium fluoride, which is the most transparent substance to ultra-violet rays known to science, happens to be extremely stable towards light. It would therefore appear that fluorine ions in a crystal lattice do not absorb any rays longer than about 125$\mu\mu$, so that photochemical changes cannot occur unless the cations have the power of absorbing light, and, of course, chemical change would not necessarily occur even then. The other halogens are all liable to react more readily under the influence of light than in the dark. Chlorine is most easily affected by the blue, violet, and ultra-violet regions. It exhibits selective absorption in the ultra-violet with a great band showing a maximum near 338$\mu\mu$. Free bromine is more sensitive to the longer wave-lengths than is chlorine, and iodine absorbs still more at this end of the spectrum. The absorption spectra of the halogens do not, however,

suffice to explain the mechanism of photo-halogenation. All that we can say is that, consequent upon the absorption of light-energy, either halogen or other reactant (or both) is converted to a state or activated phase which the energy increment has endowed with enhanced reactivity. The lack of precise knowledge as to the mechanism of the process of photo-chlorination makes the presentation of the subject somewhat difficult, as there is no criterion for judging the relative importance of different sets of empirical observations.

Let us first consider the work of Bedford[23] on the chlorination of methane. He found that chlorine would react readily, without explosion, with seven times its volume of natural gas, when illuminated by means of the white flaming arc. As the products of reaction diluted the residual gas, the reaction slowed down, and fresh quantities of chlorine would not react completely without the application of heat. Natural gas was confined in a bell-jar over water through which chlorine was bubbled, and if the mixed gases were only exposed to diffuse daylight for a short time, no reaction occurred, provided that the chlorine content was low. Under these conditions exposure to the light of the flame arc brought an instantaneous expansion of the gases. On shaking, the hydrogen chloride formed in the reaction dissolved in the water, and any products liquid at room temperature were condensed. A small percentage of natural gas was always left unchanged. Cooling of the reactants was found to hinder the formation of carbon tetrachloride. Bedford took an eight-litre Woulfe's bottle and removed the bottom; a large block of ice was then shaped out so that it nearly filled the bottle, and the whole was then placed in a water trough. Taking seven parts of methane to one of chlorine and subjecting the gases to the light from the flame arc through the glass sides of the Woulfe's bottle a brisk reaction was observed. Among the products were carbon tetrachloride in small amounts, and much larger quantities of methylene chloride and chloroform. A larger scale experiment in which up to

30 cubic feet of gas were consumed per hour gave several gallons of liquid products.

The following compositions were found :

	Liquid separating out under water layer. Percentage.	Liquid soluble in water and separated by distillation. Percentage.
Methylene chloride	35	60
Chloroform	35	28
Carbon tetrachloride	5	1·5
Chloroethanes	20	6

The portion of the products of the reaction which dissolved in water amounted to about 14 per cent. of the resultants.

Tompkins[3] observes that by distilling coal at about 500–600° C. the resulting gas is rich in ethane. This substance and also a little ethylene are separated out by liquefaction, and the liquids are allowed to evaporate. The gases are then mixed with a carefully regulated amount of chlorine and exposed to the light of a quartz-mercury vapour lamp. Chloroethanes and hydrogen chloride are formed. Leiser and Ziffer[13] have worked out the conditions for obtaining methyl chloride as the principal product of the photo-chlorination of methane. One volume of methane and six volumes of chlorine are passed through cooled chambers and exposed to the mercury arc, and small amounts of water and hydrogen chloride vapours are introduced into the reacting system, since these substances tend to prevent the formation of products other than methyl chloride. The methyl chloride vapour is first treated so as to remove hydrochloric acid and other substances, and is then liquefied. The efficiency of the reaction is 85 per cent. calculated on chlorine appearing as methyl chloride.

Snelling[10] has taken out several patents for technical methods designed to secure efficient photo-chlorination of hydrocarbons in the vapour state. In one of these it is claimed that by passing the gases backwards and forwards between transparent baffle-plates, and by placing a mercury vapour lamp at one end of the apparatus, the variations in light intensity which result from this arrangement greatly

assist in obtaining smooth controllable reactions. Snelling obtained carbon tetrachloride and chloroform in this way. The idea of baffle-plates with their double function of securing reductions in light intensity and of assisting in the mixing process has also been extended to chlorination of liquid hydrocarbons.

An elegant piece of apparatus for photo-halogenation is described by Keyes [12] (Fig. 19). A quartz-mercury vapour lamp of the straight-tube type is fitted with a jacketing tube having a condenser, a vent, an inlet and an outlet tube. The whole apparatus may be made of fused silica.

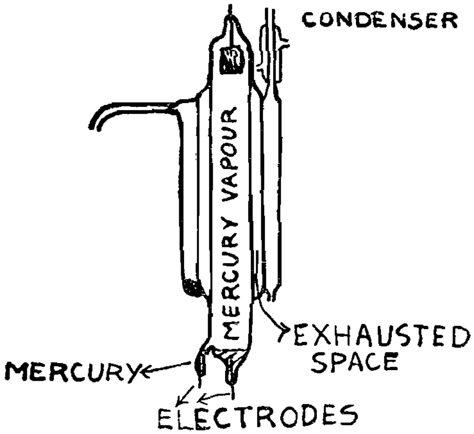

FIG. 19.

Between the lamp and the outer jacket a second tube may be used, and the first annular space exhausted to prevent undue heating of the reactants in consequence of the great heat of the arc. The method of operation is clear from the figure. It will be seen that the apparatus is well adapted for continuous processes.

When methylene chloride, water, and chlorine are exposed in a closed vessel to ultra-violet light it is claimed by Lacy [28] that chloroform and hydrochloric acid are formed. The water forms a layer above the methylene chloride, and the hydrogen chloride formed as a result of the reaction dissolves in the water. The light source is a vertical mercury

lamp, and it is placed to project upwards through the bottom of the chamber.

A number of patents (see p. 123) have been taken out for the chlorination of hydrocarbons by means of light. No useful purpose can be served by describing all the different types of apparatus in detail. The following points are, however, certainly of importance: (*a*) If the reaction is best carried out by means of the quartz-mercury vapour lamp it scarcely seems advisable to use reaction vessels made of stout glass, as a great deal of the actinic light of the lamp is thereby filtered off. This somewhat obvious precaution seems to have been disregarded on many occasions. (*b*) Stirring devices are essential with liquids undergoing photo-chlorination, as the first few millimetres of a liquid rich in chlorine absorb most of the actinic rays. (*c*) Cooling devices are necessary in most cases. (*d*) Arrangement must usually be made for the reception of the hydrochloric acid formed in the halogenation process.

It will be found that the diagram given below illustrates some of the points mentioned.

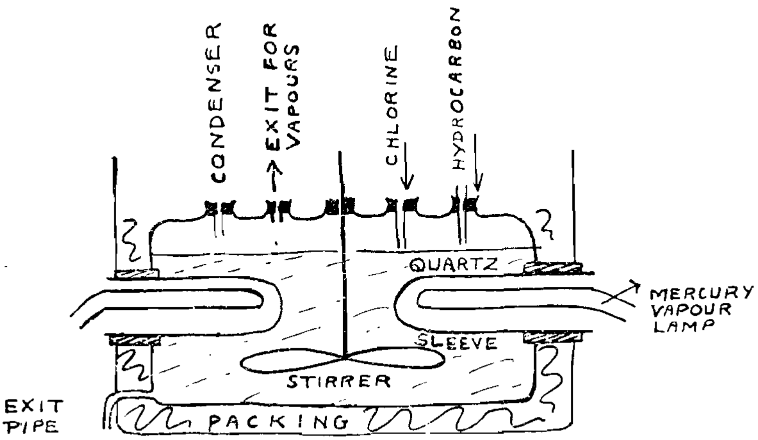

FIG. 20.

Brooks, Essex and Smith[7] have chlorinated liquids such as gasoline, petroleum oils, benzene, and toluene in a special apparatus, employing light from a nitrogen-filled

tungsten lamp or a mercury vapour lamp. If the lamp is placed at the top of the vessel and the chlorine is introduced at the bottom, the actinic rays will penetrate a considerable depth of liquid and the chlorine will slowly diffuse upwards. The maximum reaction will thus take place at a position in which the hydrocarbon is in great excess, and this will tend to restrict the reaction to the formation of monochlor products. When about 30 per cent. of the gasoline or other hydrocarbon has been converted to the corresponding monochlor compound the reaction is stopped and the products separated by fractional distillation. The unchanged hydrocarbon may then be returned to the reaction chamber and the process repeated, or else if it is desired to obtain the dichlor derivatives the monochlor compounds may be used as a starting-point for further chlorination in the same manner. Solid hydrocarbons may be melted or dissolved in carbon tetrachloride, and the same process of photo-chlorination will be found to be effective. Boyd [9] and Rodebush,[29] and also Okimaka and Sakai [11] have described alternative forms of apparatus suitable for photo-chlorination. It is interesting to find yet another example of the similarity of the silent electric discharge to ultra-violet light (*cf.* p. 74) in the experiments of Pfeifer and Szarvasy.[2] These authors found that mixtures of chlorine and hydrocarbons in the form of vapours underwent chemical reaction in the silent electric discharge.

A method of catalytic photo-chlorination has been described by Payne and Montgomery.[31] A hydrocarbon oil (shale oil or a paraffin, b.p. 230° C., or other oils mixed with powdered coal) is treated with chlorine at about 150° C. The gas is led in at first slowly, and then more rapidly, until the product is a porous black solid and hydrochloric acid gas has ceased to be evolved. Chlorine and a moist hydrocarbon vapour are led over the catalyst in the proportions of three to one, and the temperature in the reaction vessel is maintained at about 150° C. The process of chlorination is completed by passing the products of the

reaction through fused silica tubes exposed to the light from a quartz-mercury lamp. The gases are cooled to separate methyl chloride, and the liquid products are treated with sodium hydroxide to remove hydrochloric acid, and are then steam-distilled. A clear liquid results, which contains products varying in boiling-point from 57° to 193° C.

Chloroform and especially carbon tetrachloride are frequently used as solvents in photo-chlorination reactions. It is therefore of considerable interest to know how these compounds themselves behave towards light. Chloroform is rather unstable, especially towards ultra-violet light. No reaction occurs between chloroform and chlorine in the dark, and but little in the presence of light free from rays shorter than $400\mu\mu$. Beyond this point, and particularly in the region $300–340\mu\mu$, chlorination begins to occur and carbon tetrachloride can be formed quantitatively if sufficient time is allowed.

Carbon tetrachloride presents an interesting problem from the point of view of photochemistry. Benrath and Hertel[25] found that under the action of light commercial or even ordinarily purified carbon tetrachloride absorbs chlorine. If, however, the material had been previously subjected to the following rather rigorous process of purification :

(*a*) treated with chlorine for a lengthy period at its boiling-point,
(*b*) treated with nitric acid,
(*c*) treated with sodium carbonate,
(*d*) washed, dried, and redistilled,

there is no absorption of chlorine, but on the contrary a very slow liberation of chlorine. Massol and Faucon have shown that ordinary "pure" carbon tetrachloride contains traces of carbon bisulphide. These observations are of interest in connection with the proposal that the liberation of chlorine from the tetrachloride is a reaction suitable for the purpose of actinometry (see p. 56). There is, however,

no doubt that the amount of decomposition is not great enough to interfere in the study of the photo-chlorination of solutes. Benrath and Hertel investigated the rate of chlorination of various compounds dissolved in carbon tetrachloride, and as their work is of some importance the main results will be quoted.

"The solutions contained about 0·5 per cent. of chlorine. It was found that (1) absorption of chlorine does not usually begin at once, (2) after the period of induction the chlorination proceeds either at a rate proportional to the time or in some cases to the logarithm of the time, and (3) the reaction proceeds until one atom of hydrogen is displaced. There is now (4) a second induction period, and afterwards (5) a second atom of hydrogen is displaced frequently much more rapidly than the first."

Tetrachloroethane resists the action of chlorine for three hours, whilst chloroform, after an induction period of half an hour, absorbs 70 per cent. of the chlorine required for its complete conversion into carbon tetrachloride. Acetic acid, acetyl chloride, and iso-butyric acid form monochlor compounds. In the case of *n*-butyric acid two atoms of hydrogen are displaced, both at the logarithmic rate, the second induction period being quite definite.

In the case of ethyl ether, one atom was displaced at the linear rate, and after slowing down a little the absorption of chlorine went on again, the second hydrogen atom being attacked at the logarithmic rate. Propionic acid and ethyl malonate behaved similarly. Acetic anhydride was anomalous, since although two separate processes could be very sharply distinguished, on account of a long induction period, neither the linear nor the logarithmic law was obeyed. It would be of great interest to have the work of Benrath and Hertel repeated under carefully controlled conditions. It might be possible by means of screening experiments to specify the effective wave-lengths, but the use of monochromatic light will unfortunately involve almost prohibitively long periods of irradiation.

Methyl sulphate has been shown by Volmar [26] to undergo chlorination at room temperature under the influence of ultra-violet radiation. The reaction proceeds rapidly with an intense source such as the mercury arc, but the light from a metal filament lamp will slowly bring about the formation of methyl chloromethyl sulphate. This compound is the only one formed in any appreciable quantity.

Carr [30] states that the preparation of diphosgene involves the chlorination of methyl formate for about a week under the action of the light from Osram lamps of 4,000 candle-power. Curtis [21] found that the photo-chlorination of acetic acid (glacial) to the monochloracetic acid required a considerable intensity of ultra-violet light, since an iron arc at 3 cm. was effective, and the light from a projection lantern ineffective.

The chlorination of benzene homologues opens up new possibilities of complications, as, of course, the halogen may enter either the ring or the side chain or both. Gook and Eggert [20] state that at a temperature of 105° to 110° C. the product of the interaction of chlorine and toluene is very largely benzyl chloride, irrespective of whether the reaction be conducted in the dark or in the presence of light, so long as chlorine carriers such as ferric chloride are excluded. In the presence of ferric chloride, ortho- and para-chlortoluenes are formed. At a temperature of —80° C. and in complete darkness pure chlorine and pure toluene do not interact, but even at this temperature, in the presence of visible light, reaction occurs at a rate much greater than would be expected on the basis of the Einstein law of photochemical equivalence.

Gibbs and Geiger [4] have investigated the chlorination of toluene in some detail. The ordinary method of passing the gas into the boiling liquid until a definite weight of chlorine has been absorbed results in the formation of a mixture consisting largely of benzyl chloride, but also containing substances with chlorine in the ring. Toluene vapour in the presence of a considerable excess

of chlorine and a catalyst reacts to form a mixture containing :

benzyl chloride,
benzal chloride,
benzotrichloride,
chlortoluene,
chlor-benzyl chloride.

When the toluene is in excess, the presence of a catalyst and the use of light bring about the formation of benzyl chloride; but this is not very satisfactory, owing to the expense of separating the chloride from the excess of toluene.

The essential point in the patent of Geiger and Gibbs is that under the influence of *ultra-violet* rays the theoretical proportions of toluene vapour and chlorine gas react almost completely to form products chlorinated in the side chain. By regulating the rate of flow of the gases and the proportion of chlorine employed, it is possible to obtain benzyl chloride, benzotrichloride, or benzal chloride. Ellis [16] describes an apparatus specially designed for the production of benzyl chloride.

A significant observation has been made by Mott and Bedford,[24] in comparing the relative efficiencies of the white flame arc and the quartz-mercury lamp from the point of view of chlorination. The evidence shows that " a large share of the actinic power of the quartz lamp lies in the ultra-violet rays which are not necessary or even desirable for chlorination purposes."

This statement is at first sight in contradiction with the work of Gibbs and Geiger. The two sets of observations may possibly be reconciled if we remember that the great absorption band of chlorine lies on either side of $338\mu\mu$, a region covered by carbon arcs as well as by mercury lamps. Moreover, wave-lengths within the band are transmitted by glass. Mott and Bedford seem to regard all rays shorter than $400\mu\mu$ as ineffective in photo-chlorination, but it would not be safe to accept this view too literally. At any rate,

those reactions which occur in the silent electric discharge as well as in ultra-violet light seem outside the scope of the views of these authors, since the peculiar effect of the discharge is in giving very short ultra-violet rays (*cf.* p. 79).

Iodine derivatives of paraffins (except methane) may be made by mixing the hydrocarbons with iodine in the dark and subjecting the mixture either to the action of short-wave ultra-violet light or to the silent electric discharge.

Le Blanc and Aldrich [19] investigated the photo-bromination of toluene in an atmosphere consisting of oxygen 96 per cent. and nitrogen 4 per cent. The yield of benzyl bromide was independent of the intensity of the light, and was constant throughout the entire portion of the spectrum investigated. The speed of the reaction decreased with decreasing wave-length, and scarcely any reaction occurred with those shorter than $300\mu\mu$. Bromination of toluene in ethyl acetate solution is not affected by light, owing to pronounced association of the bromine with the acetate.

In the presence of catalysts such as ferric chloride or stannic chloride, benzene chlorinates readily. The list of similar reactions involving photo-chlorination and photo-bromination can be extended by consulting the larger treatises on organic chemistry. Sufficient has, however, been said to indicate the general position, which it must be admitted is somewhat unsatisfactory.

The study of the wave-lengths effective, of the nature and significance of the induction period which so often occurs and of the influence of the presence or absence of air or oxygen, may be regarded as the more promising lines of investigation.

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Section V.—THE PHOTOGRAPHIC AND ALLIED INDUSTRIES

In spite of the advent of new industries dependent on photochemical processes, the photographic industry remains and is likely to remain in the future the most developed branch of applied photochemistry.

A bird's-eye view of the processes involved in the production of a finished print will indicate the points of contact with the present work :

Preparation of Plates and Films

Glass : Celluloid : Silver halides	Photochemistry Colloid chemistry Sensitometry Synthetic dyes

Exposure

Cameras : Lenses	Actinometry (exposure meters)

Obtaining Negative

Development Fixation Washing Intensification Reduction	The latent image and its treatment

Obtaining Positive

The visible image

Preparation of Emulsions for Positives
(Papers, Lantern Plates, Films)

Printing-out papers Gaslight and bromide papers, toning, staining	Visible image Latent image
Process Work	**Colour Photography**
Chemistry of bichromated colloids and light Colour printing	Dye Chemistry Spectroscopic research

Finishing
(glazing : mounting)

The starting-point in photographic chemistry is the effect of light on silver halide. The change may be visible or invisible, the latent image being in the latter case "developed" by a kind of catalysis. Considering first the production of a visible change, it is found that although the sensitivity depends on the environment and previous history of the preparation, the silver halides darken in the order chloride, bromide, iodide, the last named being the most readily affected. Halogen absorbents sensitise the reaction, a fact which is utilised in daylight printing paper (P.O.P.) by the incorporation in the emulsion of silver nitrate or a salt of an organic acid, *e.g.* silver citrate. Printing-out papers using silver bromide, and some of the special papers used for exposure meters, contain sodium nitrite as the halogen absorbent. The visible change in silver halides does not readily occur in a vacuum.

With increasing exposure, silver chloride passes successively through the colours lilac, violet, and slate grey. Chlorine is at first liberated rapidly and then more slowly. After six months a loss of weight amounting to 8 per cent. can be observed if the chlorine is allowed to escape.

The coloured compounds were formerly regarded as sub-halides of the type Ag_2Hlg, and it was later thought that they consisted of solid solutions ($AgHlg$-Ag_2Hlg). The view favoured at the present time is that the coloured materials consist of colloidal solutions of free silver in silver halide.

The reaction:

$$4Ag\,.\,Hlg \xrightarrow{\text{light}} 2Ag_2Hlg + (Hlg)_2$$

is largely hypothetical, since the compounds Ag_2,Cl, Ag_2Br, and Ag_2I have not been isolated. The existence of these compounds has been inferred on the basis of analogy with silver sub-fluoride Ag_2F.

The anomalous behaviour of fluorine as a halogen is so well known that the risk of such an analogy is patent. The investigations of Carey Lea supplied evidence for a belief in the existence of solid solutions of sub-halides in

halides. This brilliant worker obtained synthetically a range of products showing a variable silver : halogen ratio, and resembling the photo-halides both in respect of colour and chemical properties. Carey Lea concluded that the silver present in the photo-halides existed as one or more of a series of allotropic modifications. The "allotropic" forms of silver are now regarded as colloidal particles of silver, and the photo-halides as adsorption complexes of silver with silver halide.

Complexes richer in chlorine than the so-called sub-chloride Ag_2Cl have the property of acquiring the colour of the light to which they are exposed, and a spectrum can be reproduced in colour. Unfortunately for colour photography the sensation of white defies reproduction. In this way the effect is in a sense fortuitous, and in all probability is connected with variations in the size of colloidal particles.

The foregoing considerations apply to the production of a visible colour-change in silver halides. It does not follow that the chemical and physical changes involved in the formation of the latent developable image are necessarily of the same nature as those involved in the formation of a visible image.

The mechanisms which have been proposed for the production of the latent image may be shown diagrammatically.

THEORIES OF THE LATENT IMAGE

Chemical		Physical	
Subhalide Formation	Silver Formation	Photoelectric effect	Mechanical disintegration of halide or
Silver "Germ"		Colloid silver	Depolymerisation (AgHal) $=m$(AgHlg)

The sub-halide theory of the visible image is modified so that the latent image is "developed" by the use of reducing agents such as pyrogallol and hydroquinone, which act preferentially at those places where *incipient formation of the sub-halide* has occurred.

The silver "germ" theory postulates the formation of a tiny nucleus of metallic silver which increases in size on development. There are many reactions in solids which require an active centre before occurring to any appreciable extent, a good example being the acceleration of efflorescence in crystals by the presence of a particle of anhydrous salt. By an easy transition the "germ" hypothesis becomes the "colloid" silver hypothesis. The latent image is merely the first of a series of photo-halides, and consists of a silver-silver halide adsorption complex.

The chemical theories all suffer from an obvious defect: the amount of light which strikes an extremely "rapid" photographic plate represents an extraordinarily small *but sufficient* quantity of energy, nevertheless, the whole of our experience of energy exchanges makes it difficult to conceive a *purely chemical* mechanism with so little energy intake.

The physical theories of mechanical disruption of aggregates and of depolymerisation likewise have serious disadvantages. Apart from the fact that light more frequently effects *polymerisation* than *depolymerisation*, the conception of undissociated complexes (AgHlg) is inconsistent with the modern view, based on X-ray research, that the solid consists of a space lattice of ions bound by electrostatic forces. The effect of light on the plate has been ascribed to the liberation of electrons from the halogen ions. These electrons are regarded as neutralising the positive charge of the metal ions so that atomic halogen and atomic silver are formed.

Our treatment of the problem of photographic sensitivity leaves us so far in the position that while there may be an element of truth in the idea that the photo-halides are silver-silver halide adsorption complexes, the other theories are mainly wrong. Let us consider the question more constructively. The photographic emulsion is heterogeneous, it consists of minute aggregates of crystalline silver halide dispersed in a colloidal medium such as gelatin. The number of silver halide grains may vary from 500 to 5,000 millions

per square inch. Inconceivable as it may sound, it has been possible in recent years to study the properties of individual grains.

We may first recapitulate to some extent by noting some experimental facts:

(*a*) Silver halides darken on exposure to light.
(*b*) Halogen is set free.
(*c*) The darkening is accelerated by the presence of halogen absorbents.
(*d*) Sub-halides cannot be proved to have real existence.
(*e*) Hartung has shown by very beautiful experiments that the liberation of halogen from irradiated silver halide proceeds continuously, there being no break at the point corresponding with the stoicheiometric relation :—2Ag : Hlg.

The question may now be asked whether there is any definite evidence in favour of the belief that the photo-halides consist of solid solutions of colloidal silver in the silver halides.

R. Feick and J. Schaum[1] succeeded in proving that the dielectric constants of thallous chloride, silver chloride, and lead chloride increase markedly with increasing exposure to light. In conjunction with quantitative analysis of the photochemical products, this fact indicated a direct decomposition:

$$\text{Metal . Halide} \rightarrow \text{Metal} + \text{Halogen}$$

without formation of sub-halides. In the case of silver chloride, brief exposures brought about no measurable effect. Hartung's work has been confirmed by P. P. Koch and B. Kreiss.[2] Grains of silver halides prepared in a variety of ways were suspended by means of an electrical field between the plates of a condenser and the light from a pointolite lamp focussed on them. Silver bromide lost about 25 per cent. of its weight, silver chloride rather less, and silver iodide showed no loss at all. Koch and Vogler[3] have made a contribution of fundamental importance.

If the formation of the latent image is due to the passage of an electron from the bromine ion to the silver ion, with consequent separation of free silver, the crystal lattice of the silver bromide should suffer derangement.

This view has been tested by means of Koch's arrangement of the Debye-Scherrer powder method for the investigation of crystal structure.

Measurements were made with :

(*a*) Silver bromide separated in red light from a dry plate.
(*b*) Silver bromide prepared by precipitation (*i.e.* free from gelatin).
(*c*) Silver bromide exposed either to sunlight for a day or under 5 per cent. sodium nitrate solution for 90 minutes.
(*d*) Metallic silver.

Only two crystal lattices were indicated, namely, the silver bromide and silver lattices. The spectrum of the light-darkened halide showed that the rings due to silver are superimposed on the bromide rings. The X-rays themselves do not form a visible image even after prolonged exposure. There is thus no evidence whatever of a sub-halide. The rings of the silver lattice were obtained with great clearness in a photograph of a dry plate which had been exposed in sunlight and fixed in an acid bath without development. The amount of absorption of X-rays by a plate so treated, corresponded after correction for the absorption of the gelatin, with a free silver content of 0·00024 grams per square centimetre. Similar results were obtained with silver chloride, but no indication of the silver lattice was found in silver iodide even after daily exposure to sunlight for four months. From the evidence now available it would seem to be proved that the conception of a silver-silver halide adsorption complex gives a reasonable idea of the nature of a photo-halide.

Silver bromide prepared by precipitation with excess of silver nitrate is more sensitive than silver bromide formed

in the presence of excess of alkali bromide. We may picture the change as follows:

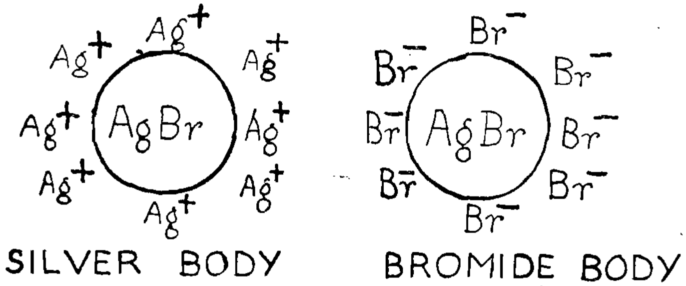


FIG. 21.

since in a silver bromide sol the particles are positively charged if silver ions are present in excess.

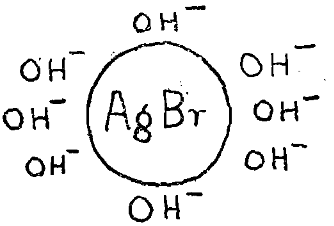
Sensitivity thus appears to be related to the adsorption of silver ions, and the action of light may be photo-electric in the sense that the neutralisation of the positive charge on the silver ions may result in something akin to coagulation of a colloid.

The coarser particles with adsorbed atoms of silver may thus act as nuclei in the process of development.

The two kinds of silver bromide may be spoken of as "silver-body" (Ag-body) and "bromide-body" (Br-body) respectively.[4]

Fajans and Frankenburger[5] have shown that apparently amorphous silver bromide has a lattice structure such that each silver atom is surrounded by six bromine atoms, and each bromine in turn by six silver atoms. If the action of light is to cause the transfer of an electron from a bromine ion to a silver ion, the silver-body should be more sensitive than the pure bromide. Now it has been shown that pure silver bromide dried in vacuo at 300–350° darkens with light between 425 and 490$\mu\mu$ when mercury vapour is present as halogen acceptor. Longer wave-lengths bring about no change. On the other hand, the silver-body, using the excess of silver nitrate as acceptor, darkens with light on the long-wave side of 615$\mu\mu$ and bromine is liberated.

Fajans and Steiner have investigated the silver—and chloride—bodies of silver chloride. Similar results were observed, but the difference in spectral sensitivity was not so marked as in the case of the silver bromide bodies. With Frankenburger, Fajans has found that when the well-washed bromide body is exposed under alkaline solutions it darkens under red light, without liberation of bromine. Hence it would appear that a substance analogous to silver hydroxide undergoes decomposition.



HYDROXIDE BODY

Fig. 22.

In support, it has been observed that pure silver oxide is sensitive over the same region of the spectrum as is the bromide-body under alkaline conditions. Probably, therefore, it is the silver hydroxide which is decomposing at the surface of the silver bromide. Another interesting discovery has been made by Fajans and Frankenburger concerning the sensitising effect of nuclei of metallic silver.

With light of wave-lengths on the short-wave side of $490\mu\mu$ both pure silver bromide and the bromide body undergo photochemical change with liberation of silver. If the exposed emulsion or preparation is now exposed a second time, but on this occasion using wave-lengths on the long-wave side of $560\mu\mu$, it is found that darkening occurs, *i.e.* that the pre-exposure has endowed the plate with panchromatic sensitivity (see p. 137).

As has already been pointed out, photochemical change only occurs by virtue of the absorption of light The spectrum of silver bromide shows negligible absorption on the red side of $500\mu\mu$, but since the silver body is sensitive to red light the absorption of rays at $615\mu\mu$ can no longer be negligibly small. How is the necessary change in absorption spectrum brought about?

Fajans assumes that the electronic orbits are distorted in consequence of the attractions of positively charged

adsorbed silver ions. The deformation will effect a "polarisation which will be reflected by a change in optical properties" (refraction, absorption).

A fairly consistent picture is thus obtainable of the mechanism operating in the formation of the visible image. The latent image is a more difficult matter.

F. C. Toy, of the British Photographic Research Association, has recently (*Nature*, Sept. 24, 1927) made a valuable contribution to this subject. His arguments may now be summarised very briefly. A distinction is first made between the photo-electric and photo-conductivity properties of silver halides; the former consists in the *complete* liberation of the electrons, and the latter in the freeing of electrons internally (an internal photo-electric effect) resulting in a change in conductivity. Now, since the photographic action in a bromide emulsion takes place with wave-lengths much longer than the longest capable of producing photo-electric emission from silver bromide, the photographic mechanism cannot be photo-electric (*cf. Phil. Mag.*, 1927, **3**, 482).

The effects of light of different wave-lengths run closely parallel for the photographic and photo-conductivity effects, for example, a slow silver bromide emulsion (process plate) shows zero sensitivity at wave-lengths greater than $500\mu\mu$, and Coblentz has shown that the photo-conductivity becomes measurable with light of the same wave-length. Both the photographic and photo-conductivity effects are increasingly strongly exhibited as the wave-length decreases; but whilst the process plate readily records all wave-lengths between 500 and $220\mu\mu$, the photo-conductivity effect falls to zero at $420\mu\mu$, after passing through a maximum. Now, with thinly coated photographic plates the photographic sensitivity of silver bromide increases on passing from the violet to the ultra-violet, and it has now been shown that for a layer 0·07 mm. thick the photo-conductivity of silver bromide is twice as great at $365\mu\mu$ as at $436\mu\mu$. "Thus," says Toy, "the greatest difficulty in the way of demonstrating the identity of the photographic mechanism and

that which produces a change of electrical conductivity on illumination, has been removed." It would appear that the formation of the latent image involves the transfer of valency electrons from bromide ions to silver ions, resulting in the formation of metallic silver and free bromine.

Let us consider the evidence in favour of the view that the latent image consists of free silver. In the first place, the latent image strongly resists destruction by means of nitric acid, so that if it consists of metallic silver it must be protected in some way. On the other hand, chromic acid, which also dissolves silver, will convert a very sensitive (fast) plate into a relatively insensitive (slow) plate implies the necessity for some metallic silver *before* exposure. That it is present in the latent image seems to be proved by the following experiment. A plate is exposed and then fixed. After washing it is immersed in a solution containing a silver salt and a reducing agent, with the result that an image appears. Now this treatment can only result in the deposition of silver on silver nuclei; so that exposure to light seems definitely to cause the formation of specks of metallic silver. Extremely small particles of silver are probably formed in the manufacturing process for rapid plates, but in the unexposed plate they remain too small to be developable.

This does not preclude them from catalysing the photochemical deposition of somewhat larger specks which would in turn catalyse the development of the halide grain.

A good deal of progress has hinged on a striking observation by Clark, who found that a solution of sodium arsenite caused the formation of a latent image in the absence of light. A statistical study of the observations showed that centres of development in the grains came into operation in exactly the same way, irrespective of whether the exciting agency were light or the solution of sodium arsenite. This observation lends support to a suggestion that some "*X*-substance," differing from silver halide, is present in the unexposed plate, and that it is moreover unevenly distributed. Wherever it is locally concentrated the

incident light is effective, and a centre for development is formed. If the "*X*-substance" can be removed, it should be possible to convert a fast plate into a slow plate. Clark carried out this experiment in an elegant manner by giving the plate first a brief exposure followed by treatment with chromic acid solution when the plate became very slow to subsequent exposure. This experiment is interpreted to mean that the process of forming the latent image causes the "*X*-substance" to be less tightly adsorbed. This loosening renders it more rapidly "soluble" (removable). The discovery of the nature of this "*X*-substance" has proved a formidable task, but the problem has been triumphantly solved by combined work in the Kodak Laboratories. The line of attack was to consider another variable in the photographic emulsion, namely, the gelatin. S. E. Sheppard found that some samples of gelatin favoured the production of sensitive emulsions, whilst other samples gave relatively insensitive preparations. Inert gelatins could be "activated" by inoculation with minute quantities of a gelatin "*X*." This material was prepared by taking the acid de-liming liquors from the gelatin manufacturing process and precipitating with aluminium hydroxide. The dried alumina was treated with solvents such as alcohol, ether, or ligroin, and the extract was found to be rich in the "*X*-substance."

A variety of products was next examined to see whether the "*X*-substance" was present or absent, and positive tests were obtained with preparations from the seeds and hulls of beans, peas, cereals, and lucerne. Black mustard seeds proved to be an especially rich source. Finally the unknown substance was identified as allyl mustard oil or allylthiocarbimide, C_3H_5NCS. Concentrations as low as 1 in 1,000,000 of this substance can render inert gelatin quite active. Allyl thiocarbamide, $C_3H_5NH.CS.NH_2$, is also active. Compounds in which the sulphur exists in the form found in mercaptans, or in which it forms part of a ring are inactive.

Allyl thiocarbamide forms an insoluble complex,

$(AgBr)_m.(C_3H_5NHCSNH_2)_n$, with silver bromide. In alkaline solution this complex breaks down with resultant formation of silver sulphide, which is deposited as minute specks on the surface of the grain. Selenium and tellurium compounds of a similar nature also function as sensitisers. In general, sulphur, selenium, and tellurium form active compounds, provided that the atoms of these elements are doubly bound with another atom and not singly linked to two other atoms.

Sheppard, Trivelli, and Loveland [7] have endeavoured to explain the mechanism of silver sulphide, telluride, and selenide in acting as sensitisers. According to these authors the sole function of the specks of sensitiser is to collect about them the silver atoms produced in the photochemical decomposition of silver bromide, so that ultimately a developable aggregate is formed. It is regarded as highly probable that the silver nucleus must exceed a certain minimum in size before development can occur. The Kodak researches are covered by British patents Nos. 235209, 235210, 235211, of June 6th, 1924.

The following types of compounds are enumerated as effective: thiocarbimides (alkyl, aryl, acyl), thiocarbamides (alk-oxy, aryl-oxy), allyl-*iso*thiocyanate, phenyl-*iso*thiocyanate, phenyl-thiocarbamide, thiocarbamide, thio-semicarbazide, sodium thiosulphate, di-*o*-tolyl-thiocarbamide, allyl-*iso*-selenocyanate, potassium tellurocyanide, allyl-telluro-carbamide. It is claimed that the use of any of the above compounds enables inert gelatin to be converted into active gelatin, and enables the ripening steps in the preparation of emulsions to be dispensed with either wholly or in part.

Rawling, of the British Photographic Research Association, has obtained independent confirmation of these views, although some of his results demonstrate quite clearly that a completely satisfactory theory of photographic sensitivity, covering all the facts, is not yet available.

According to the Einstein law of photochemical equivalence, $h.\nu = h.c/\lambda$, where λ is the wave-length of the light and $h\nu$ is the corresponding quantum of energy. As λ

increases ν decreases, so that the quantum of red light is smaller than the quantum of ultra-violet light. The photochemical efficiency of the photographic plate is greater in the ultra-violet than in the red, a result which would appear unexpected at first sight. When, however, it is recalled that only the light absorbed is photochemically effective, the absorption spectrum provides a partial explanation, although for reasons not yet clear the variation of photochemical effect with wave-length rarely runs parallel with the absorption curve. The absorption may be determined accurately by means of spectrophotometers (see p. 271), but for photographic technique the wedge spectroscope (see p. 271) gives sufficiently precise results, besides giving a less ambiguous picture of spectral sensitivity.

The curves of spectral sensitivity of plates or papers are obtained by the use of a uniform source of light placed in front of the slit of a spectroscope using a wedge of non-selectively absorbing material. The negative indicates the sensitiveness of the plate in various regions.

In printing papers the sensitivity of silver chloride reaches a maximum in the violet near $420\mu\mu$ and falls off rapidly in either direction, whilst in the case of the bromide the maximum is near $370\mu\mu$, and for the iodide near $440\mu\mu$. When a latent image is to be developed the wave-lengths of maximal sensitivity are at $375\mu\mu$ for the chloride and $460\mu\mu$ for the iodide, whilst the bromide shows a flat maximum over the region $370–450\mu\mu$, and the sensitivity extends to an appreciable extent into the red region.

As long ago as 1840 E. Becquerel observed an interesting effect in his work with daguerrotypes. In Daguerre's process a plate of silver was first treated in the dark with iodine. On exposure, the light brought about the formation of free silver, which could then be amalgamated by contact with mercury vapour, with the result that a visible image appeared. Becquerel found that the latent image produced by blue light became visible on exposure to red and yellow light. In the same way, if the plate was first exposed to blue light for a brief period and a photograph was then

taken, using red light, the image became developable by means of mercury vapour. The mechanism of this effect is clear from the fact established by Lüppo-Cramer that silver chloride in the presence of colloidal silver is sensitive to the entire visible spectrum (*i.e.* is panchromatic). The first effect of blue light is to form this sensitive silver chloride-colloidal silver complex.

In 1872, Vogel discovered that plates could be sensitised by treating the emulsion with certain dyestuffs. The extra spectral sensitivity acquired in this way is roughly parallel with the absorption spectrum of the dye, except for a slight displacement towards the red. The effective dyes are usually themselves sensitive towards light. The mechanism of sensitisation is not clear, but the following suggestions have been made:

(1) The dye fluoresces and the fluorescent light affects the plate. Unfortunately for its validity this idea is at variance with a fundamental principle in fluorescence, which requires the exciting light to be shorter in wave-length than the excited light (Stokes' Law). The validity of Stokes' Law has only been disproved for very special conditions which do not obtain here.

(2) Under the action of light the dye emits electrons (photo-electric effect) which assist in the formation of a latent image.

(3) The dye undergoes photochemical decomposition, and the resultant product or products attack the silver halide.

Vogel's discovery bore fruit in *orthochromatic* and *panchromatic* photography. The terms may be defined as the true rendering of the relative brightness of *various* or *all* colours respectively. There are two ways of achieving this effect: *either* the incident light may be screened, *or* the spectral sensitivity of the plate may be corrected. By screening is meant the selective diminution of the intensity of light of those colours which attack the plate with disproportionate readiness in comparison with other colours.

Dyed plates and light filters are frequently used in conjunction, *e.g.* a yellow screen may be used to absorb some of the violet light and the plates may be sensitised to green and yellow light.

The efficacy of a screen can be tested at once by its absorption spectrum, but the sensitising action is less simple, and, indeed, the absorbing entity is quite possibly the silver halide-gelatin-dye complex.

Only a small proportion of the known dyestuffs are effective sensitisers, but of these the amount needed is exceedingly small, a dilution of 1/400,000 being sometimes sufficient. The ideal sensitising dyestuff should result in a plate reproducing in its spectral sensitivity curve the relative brightness of different colours as perceived by the eye. Such a dye is not yet available, although an approximation to the ideal is possible.

Among the dyes used are the phthaleins which sensitise to yellow and green light:

e.g. Eosin (tetrabrom-fluorescein), in which the effect is observed in the yellow and green-yellow, but not the blue-green;

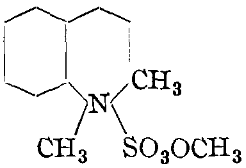
Erythrosin (tetraiodo-fluorescein), which shows a similar effect extending a little further into the green.

The blue and violet dyes of the rosaniline type, *e.g.* ethyl violet, sensitise to yellow and orange light. Quinoline red acts in the yellow and red. Cyanine (made by the interaction of alcoholic potash, amyl iodide, quinoline, and lepidine) is a moderately good sensitising agent for the yellow and orange regions.

Ethyl red (*iso*cyanine) is obtained by the action of alcoholic potash on a mixture of iodoethylates of quinoline and quinaldine, and has been used for sensitising to orange light. The blue lepidine cyanines extend the sensitivity into the red. Orthochrome T. (*p*-toluquinaldine-*p*-toluquinoline-ethyl cyanine) gives a very even sensitisation, whilst pinachrome (*p*-ethoxy quinaldine, *p*-ethoxyquinoline-ethylcyanine) sensitises up to $650 \mu\mu$. Pinaverdol (*p*-toluqinaldine, quinoline methyl cyanine) is particularly

effective in the green and yellow. König achieved something approaching true panchromatic sensitivity with pinacyanol and ethyl cyanine, both being effective to 680$\mu\mu$, and a closer approximation still with dicyanine, which is effective right to the extreme limit of visible red without causing undue predominance at the other end of the visible spectrum.

By the action of dimethyl sulphate on quinaldine, sulphomethylates are formed



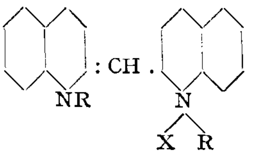
which on heating with alkali yield cyanine dyestuffs.

"Homocol" and "isocol," produced by the Baeyer Company, are of this type. The isocyanines are made by the action of alkali on equimolecular proportions of the alkyl iodides of quinoline and quinaldine. Their solutions are purple by transmitted light, whereas those of a cyanine are blue. Pinachrome, pinaverdol, and orthochrome belong to this class. The pinacyanols are prepared similarly in the presence of formaldehyde, and the dicyanines are prepared in the presence of an oxidising agent. Kryptocyanine, a condensation product of lepidine iodoethylate, acts as a remarkably good sensitiser for the near infra-red rays. Its efficacy may be gauged from the fact that up to 850$\mu\mu$ it is superior to dicyanine, but beyond 900$\mu\mu$ the advantage is with the latter.

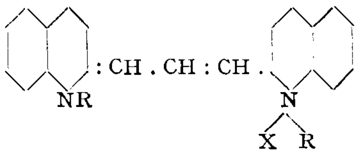
Before the war most of the photographic sensitisers were made in Germany and sold under trade names. The names chosen gave little or no guidance to their constitutions, and the patents gave only very brief accounts of the methods of preparation. The need for panchromatic plates in the Allied Forces became very urgent for photography from aircraft, and a good deal of valuable work was carried out to fill gaps in our knowledge of sensitisers.

Much progress has been made by Mills and his

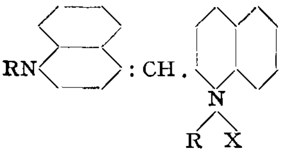
collaborators [9] in elucidating the nature of the cyanine dyes.



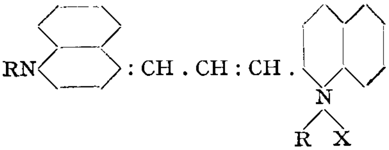
2 : 2′ Cyanines (Pseudocyanines).



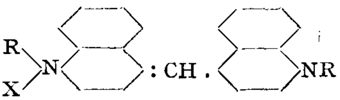
2 : 2′ Carbocyanines (Pinacyanole).



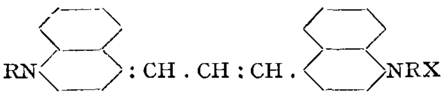
2 : 4′ Cyanines (iso-Cyanines).



2 : 4′ Carbocyanines (Dicyanine).

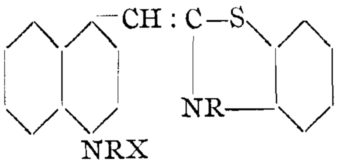


4 : 4′ Cyanines (Cyanines).



4 : 4′ Carbocyanines (Kryptocyanine).

Braunholtz and Mills describe a series of dyes intermediate between thiocyanines and iso-cyanines, which they call thio-iso-cyanines

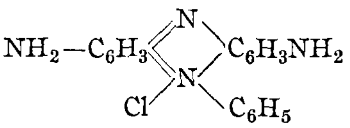


In the form of iodides they act as powerful sensitising agents for the green as far as 580$\mu\mu$.

Increased spectral sensitivity and the approach to true panchromatism brought difficulties of dark-room manipulation in their trail. The ruby light which had been found effective in avoiding fogging of ordinary plates was too bright for orthochromatic plates, and useless for panchromatic plates. Coloured glass became impossible for dark-room illumination, and dyed films of gelatine or sheets

of coloured paper mounted between glass plates were chosen so as to give a very feeble glimmer of red or green light. The green screen results in a light which demands a period of dark adaptation for the eyes of the operator, but even with such feeble illumination a good panchromatic plate is very easily fogged. Absolute darkness is essential for safety.

The problem of dark-room manipulation was therefore attacked in another manner. A search was made for materials capable of decreasing the sensitivity of the exposed plate without destroying the latent image. Lüppo Cramer found a solution in the shape of the dyestuff phenosafranine

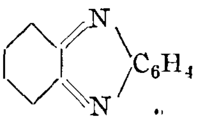


which renders panchromatic plates developable in quite a bright yellow light.

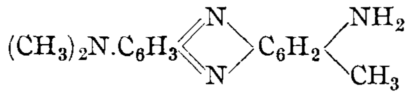
The typical desensitiser is something more than a screen in the developer. This idea had been previously tried, magnesium picrate having been added to the developer in order that its own selective absorption might hinder the transmission of actinic light to the plate.

Phenosafranine desensitises the plate against red and violet rays, although it transmits these wave-lengths fairly freely. Lüppo Cramer further showed that the desensitising action may be specific for one or other of the silver halides, *e.g.* erythrosin, pinacyanol, and pinachrome, *desensitise* silver iodide-gelatin plates, although they are used as *sensitising* agents for silver chloride and silver bromide emulsions. A. and L. Lumière and Seyewetz [10] investigated the relationship between chemical constitution and desensitising action.

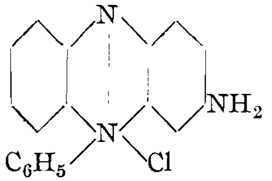
They showed the phenazine nucleus



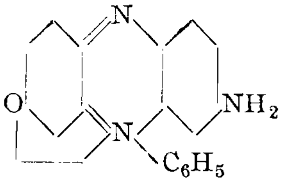
to be necessary, and that the substitution of amide groups in the benzene ring endowed the product with desensitising action, *e.g.* neutral red



Aposafranine,

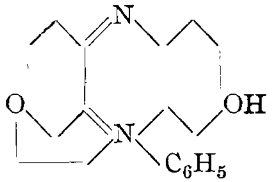


in which an amino group has been lost, and safranone,



in which the amino group has been replaced by oxygen, are much less efficient desensitisers than phenosafranine.

In safranol



where two amino groups have been replaced by oxygen or hydroxyl, the densitising action has disappeared.

Lumière and Seyewetz have also shown that phenosafranine does not form a permanent compound with either silver halide or gelatin, since any unexposed plate can recover its original spectral sensitivity after bathing with phenosafranine if washing with water is sufficiently prolonged. It seems probable that the mechanism of desensitisation involves the formation of an adsorption complex.

The normal range of spectral sensitivity for an ordinary plate is 500–220$\mu\mu$. Beyond 500$\mu\mu$ plates must be sensitised, and progress in this direction has been so great that rays up to 1·1μ can now be photographed with relative ease. Kodak "infra-red sensitive" plates give good results with short exposures up to 1·1μ. An ordinary tungsten lamp or a Pointolite gives a satisfactory intensity up to 0·9μ, and for work above 1·0μ a high intensity arc is necessary.

The loss in sensitivity on the ultra-violet side of 220$\mu\mu$ is due to the absorption exercised by gelatin. Schumann showed that plates made with as little gelatin as possible were sensitive to rays from 125$\mu\mu$ to 220$\mu\mu$. These Schumann plates are used in vacuum grating spectroscopy, and rays from 5–220$\mu\mu$ have been photographed in this way.

Ordinary plates may be partially "Schumannised" by dissolving out a large proportion of the gelatin by means of sulphuric acid. Apart from the question of expense it is not generally worth while to attempt to make Schumann plates for oneself, as they require great care in handling. Development, fixation, washing, etc., must be all carried out without any contact between the fingers and the sensitive surface.

Jeantet and Duclaux describe an ingenious method for "sensitising" plates to extreme ultra-violet rays. If a thin film of highly fluorescent mineral oil (or other suitable fluorescent material) is spread over the surface of the plate; the very short-wave ultra-violet rays cause emission of fluorescent light, which by Stokes' Law is of longer wave-length than the exciting light.

It has been found empirically that certain oils were specially suitable (*e.g.* the medical preparation "Nujol"). The author's own experience goes to show that there is little value in naming the brand and commercial specification of the successful oils, as different batches differ in respect of fluorescent effect. The principle is, however, a sound one and within limits the method is efficacious.

Fluorescence has been used to shorten the exposure in X-ray photography. Finely divided calcium tungstate ($CaWO_4$) is spread evenly and fairly thickly on a base of celluloid or cardboard and the tungstate surface is placed in close contact with the sensitive side of the photographic plate. When the X-rays impinge on the screen a bluish-white fluorescence is excited and records itself locally on the adjacent plate. The exposures necessary to secure X-ray photographs are reduced to 15–25 per cent. of the required without the use of fluorescent screen.

PHOTOGRAPHIC EMULSIONS AND COLLOID CHEMISTRY

The sensitive materials of photography are nearly all colloidal systems, the silver halide particles being dispersed in a medium such as gelatin or collodion.

For dispersed systems, the ratio of the surface area (S) to the volume (V) of dispersoid is called the dispersity.

In a mass m of specific gravity ρ, containing n particles of spherical shape,

$$4/3\pi r^3 n\rho = m$$

$$4\pi r^2 n = S$$

hence

$$S/V = S\rho/m$$

Suspensions and emulsions contain particles or droplets visible under the microscope and not smaller than $0{\cdot}1\mu$ in diameter.

In suspensoids and emulsoids the particles are between $0{\cdot}1\mu$ and $1{\cdot}0\mu$ in diameter, and are not visible under the microscope.

A colloid in "solution" is called a "sol," after precipitation in a jelly-like form it is called a "gel." In photography, dispersity or its reciprocal—grain-size—is of great importance. P. P. von Weimarn has shown that in general the dispersity goes through a maximum as the concentration of reactants is increased.

By mixing equimolecular solutions of silver nitrate and potassium bromide a clear sol is formed for concentrations

below 0·001 N. When the concentration is near 0·025 N an unstable suspension results. When the concentration is 1–2 N a flocculent precipitate results, but for very concentrated solutions a voluminous gel is obtained.

Addition of a protective colloid such as gelatin makes the dispersity independent of the concentration of the reactants over a considerable range if the gelatin content is sufficiently high. The grain-size for any defined concentration of reactants can be made to vary by altering the initial gelatin : silver halide ratio.

It is clear, therefore, that the dispersity of an emulsion will depend on the following initial conditions :

(*a*) Proportion of gelatin.
(*b*) Concentration of reactants.
(*c*) Relative concentration of reactants.
(*d*) Temperature.

Sheppard's statement that the methods used in industry for making photographic emulsions "depart considerably from those published" may be taken as authoritative, and it is therefore not proposed to consider them in any detail.

Collodion emulsions and those used in printing-out papers consist of silver halide precipitated in the presence of excess of silver nitrate, which acts as a halogen absorbent.

Emulsions which are intended for the formation of a *latent* image contain silver halide precipitated in the presence of excess of alkali halide. The dispersity is high (very fine grain) in gaslight and bromide papers and lantern slides. Emulsions designed for the production of negatives consist chiefly of silver bromide with a little iodide. The emulsion undergoes a process of ripening—digestion with excess bromide at moderate temperature—which probably results in the formation of a dispersion of colloidal silver in the halide grain.

The latent image obtained by exposing the plate may be rendered visible by two processes, viz. physical development and chemical development. In the former the black parts

of the negative gain their silver largely from the developer, whereas in the latter the metallic silver is formed from the exposed silver halide grains themselves.

Physical development is exemplified by the use of ferrous sulphate, silver nitrate, and acetic acid.

$$6FeSO_4 + 6AgNO_3 \rightarrow 2Fe_2(SO_4)_3 + 2Fe(NO_3)_3 + 6Ag$$

or

$$Ag^{\cdot} + Fe^{\cdot\cdot} \rightarrow Ag + Fe^{\cdot\cdot\cdot}$$

The metallic silver liberated is deposited on the latent image. Chemical development requires fairly powerful reducing agents such as pyrogallol and hydroquinone. The number of grains developed depends on the number which have undergone photochemical change during exposure, so that the blackening of the negative will therefore depend on the size and number of grains affected.

In measuring the efficacy of a developer the blackness of the negative is used as a criterion, and is expressed in terms of *opacity* and *density*.

I_0 (*intensity of light incident on to negative*) $\div$
I (*intensity of emergent light*) = opacity

and $$\log \frac{I_0}{I} = \text{density}$$

The density can easily be measured photometrically.

Hurter and Driffield showed that the mass M of silver is given by $D = pM$, where p is a constant (the photometric constant) for a particular type of plate and developer.

The different types of emulsions may be distinguished by the "*characteristic*" curve obtained by plotting the logarithm of the exposure (intensity $\times$ time) given to a plate against the density.

The straight line portion represents correct exposure, and its slope the development factor (γ), which is a measure of the degree of contrast. The value of γ increases with increasing time of development to a limit γ_∞, which denotes the maximum contrast attainable with the particular type of plate considered.

The straight line can be expressed by the equation :

$D = \gamma (\log_{10} E - \log_{10} i)$ where $\gamma = \tan \alpha$
and i = the intercept on the $\log_{10} E$ axis.

So long as this equation remains valid the density obtained for different degrees of development varies directly as γ.

The rationale of development is largely a question outside

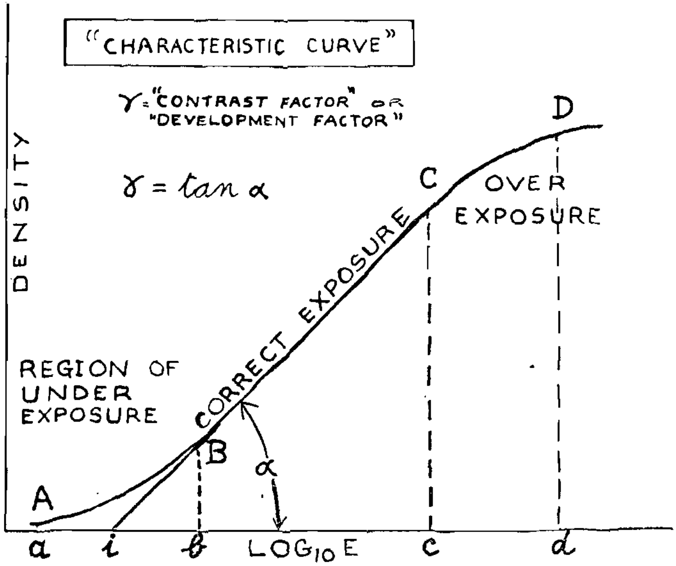


FIG. 23.

photochemistry and need not be considered in detail. The developing solution contains usually :

(*a*) Organic reducing agent (aromatic *o*- and *p*-dihydric phenols, diamines, or aminophenols).

(*b*) Alkaline accelerator (sodium carbonate, potash, or soda).

(*c*) Preservative (sodium sulphite or sodium metabisulphite).

(*d*) Restrainer (potassium bromide).

(*e*) Water.

The organic compound performs the reduction, a process which is accelerated by hydroxyl ions either directly or by

displacing the tautomeric equilibrium of the aromatic compound. Sodium sulphite retards the absorption of oxygen from the air, *e.g.* by hydroquinone or pyrogallol, and thus protects the negative from being stained by the oxidation products. The bromide prevents the formation of chemical fog.

Positives are now generally obtained by development, the old printing-out and self-toning papers tending to become obsolete. The emulsions used for positives need to be much slower, *i.e.* less sensitive than those used in the preparation of negatives, and they need to show a finer grain. Silver chloride plays a much greater rôle in these emulsions. Films for the production of cinematograph positives consist largely of silver bromide with some iodide, and are from $\frac{1}{10}$ to $\frac{1}{30}$ as fast as a process plate for negatives. Bromide papers for enlargements are still slower, whilst gas-light papers containing silver chloride and bromide may be only $\frac{1}{500}$ as fast, in order that they may not fog in a relatively bright light. Developers for positive emulsions must not be too active as reducing agencies, hence they are usually more dilute and weaker in alkali than the developers used in the production of negatives.

The efficacy of a gas-light paper is determined by the ratio of incident to reflected light, and the "characteristic" of a positive emulsion gives information just as valuable for papers as for plates.

In both negatives and positives the degree of blackening is not a simple function of exposure. Schwarzschild found that when the product of intensity of illumination into time of exposure (I.t) is constant, the density or blackness of a photographic negative was not necessarily constant. His experience is summarised in the equation:

$$\frac{I_1}{I_2} = \left(\frac{t_2}{t_1}\right)^n$$

for constant density of the negative. An alternative expression for the density S may be used :

$$S = k \,.\, It^n \text{ where n and k are constants.}$$

The significance of k has been discussed by Plotnikow (*Lehrbuch der Photochemie*, p. 667).

Schwarzschild found the value 0·86 for n, whilst other observers have obtained rather different values (Mallet, 0·846, 0·865; Robertson, 0·86; Henri, 0·90). The significance of the Schwarzschild constant is obvious in measurements of absorptive power by photographic methods. A detailed investigation of this point has been carried out by Baly, Morton, and Riding [11] (*Proc. Roy. Soc.*, 1926, A. 113, 709).

An important aspect of photography consists in evaluating the actinic efficiency of various kinds of illumination in order to ensure correct exposure.

Exposure tables are given (*e.g.* in the *Wellcome Diary*) which require the following factors:

(*a*) Weather conditions (sunny, diffused daylight, cloudy).
(*b*) Subject conditions (portrait, landscape, seascape, dark background, etc.).
(*c*) Time of day.
(*d*) Time of year.
(*e*) Latitude.
(*f*) Lens diaphragm value (stop).
(*g*) Plate speed.

The exposure time is regarded as varying inversely with plate-speed and light intensity, and directly as the diaphragm aperture. Complicated as it seems, the method has been carefully standardised by experience, and it gives exposures which are rarely outside the degree of latitude allowed by the plate.

The correct exposure may be obtained by the use of exposure meters (Watkins Wynne, etc.). In the well-known Imperial Exposure meter, a standard slip of sensitised paper is allowed to darken until it matches a standard green comparison tint and the *time* is observed. A slide rule arrangement is used which indicates correct exposure for given *times*, plate speeds, and stops, with suitable corrections for subjects of different kinds.

The speed number is expressed in various ways, that

of Hurter and Driffield being perhaps the most widely used.

The "H and D" value is obtained by multiplying the reciprocal of the inertia by 34. The inertia is the *i* of Fig. 23 in the characteristic curve of the plate, and is expressed in candle-meter seconds. Watkins took the standard 1·0 as a speed such that with full summer sun and stop f/8 an exposure of two seconds would give a "sound" negative.

Type of Plate.	H and D Speed.	Watkins.
Very slow	11	16
Slow	45	65
Medium	150	210
Fast	350	500
Very fast	700	1,000

PHOTOGRAPHY AND PRINTING

Photography is the basis of the mechanical reproduction of pictures and drawings in printed matter. There are three different kinds of printing—intaglio, surface, and relief.

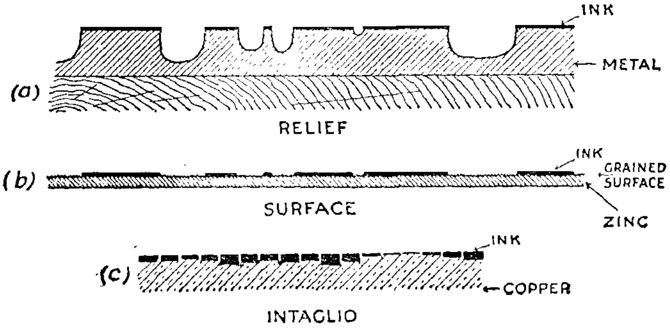


FIG. 24.

[Reproduced from "Photography as a Scientific Implement," by permission of the publishers, Messrs. Blackie and Son, Limited.]

In relief work the portions which receive the ink stand out from the others as in ordinary type, woodcuts, and half-tone blocks. In surface printing there is little relief and the inked parts of the picture are transferred to a surface

of limestone (lithography) or metallic zinc by means of a *greasy* ink. The rest of the surface is kept wet and re-inking only occurs at the greasy places. Intaglio printing is the process used with engravings, etchings, and photogravures. The ink remains in the hollows and is wiped away from the surface. Photography has been applied to the three different kinds of printing.

The first process is to obtain a very contrasty negative by copying the original picture with a suitable camera. Process plates may be used and developed with hydroquinone-potash. The plates should be "backed" (to prevent reflection from the rear surface) by means of a dark preparation, and for many purposes the negative is intensified to increase the contrast. The wet collodion process still survives in this field, but it requires a little more skill in manipulation than the dry-plate process. An ether-alcohol solution of collodion containing a mixture of ammonium, strontium, and cadmium iodides with a little of the corresponding chlorides, is spread evenly over a very clean glass plate, which has been previously covered with a thin film of gelatin. When the collodion has hardened, the plate is immersed in silver nitrate solution and silver iodide is formed *in situ*. The plate is most sensitive to blue and ultra-violet light, and the photograph is taken with arc-lamp illumination. A bright orange-yellow light may be used in the "dark" room. Development is physical (see p. 147), and the ferrous sulphate-acetic acid developer previously referred to is used. Fixation is carried out by means of potassium cyanide, a far better solvent than sodium thiosulphate for silver iodide, and the negative must always be intensified.

The next process consists in preparing the printing surfaces. This depends on one of the most important reactions which come within the purview of applied radiation, namely, the action of light on bichromated colloids.

A solution made up either from: White of 1 egg+6 grms. ammonium bichromate in 300 c.c. water, or fish glue 100 c.c.+6 grms. ammonium bichromate in 200 c.c.

water, is spread evenly and thinly over a prepared metal plate, which is then warmed until dry.

When light strikes such a plate the colloid is tanned or rendered insoluble. The mechanism of the reaction may perhaps be as follows:

$$\text{Chromic acid} \xrightarrow{\text{light}} \text{Chromium sesquioxide}$$

$$Cr_2O_3 + CrO_3 \rightarrow Cr_2CrO_6 \text{ (Chromium chromate).}$$

It is safer to say that the primary reaction is purely photochemical, and that the resultants react with the chromated colloid to form the insoluble image.

The exposed plate is dipped into water after receiving a coating of a waxy ink, and the unaffected parts of the colloid are easily detached as they swell up readily. The plate is then dusted with bitumen, which adheres to the ink but not to the clean surfaces of zinc. On drying at a moderate heat the deposit soon hardens and forms a support for the printing ink.

The process used in the preparations of line blocks can give only the white of the paper and the black of the ink. The impression of grey can only be obtained by breaking the surface into minute dots. This is effected by two plates of glass ruled with opaque lines and so arranged that the lines are at right angles, the result resembling a gauze of 50–200 mesh. This screen is placed between the lens and plate and the distances are adjusted so as to give soft shadows. The bichromate-gelatin process is now used as described.

The collotype process is rather similar. A thick surface of gelatin-bichromate is formed on glass. On exposure the gelatin is hardened, and the unaffected parts can only swell upwards, the net result being a "buckling" of the surface into tiny wrinkles. The reticulation varies with the depth of gelatin tanned by the light. An aqueous mixture of glycerol and water is used to enhance the wrinkling effect. The plate now consists of dry, hard, ink-retaining surfaces and swollen, damp, ink repelling parts. The surface is capable of giving about 1,000 copies.

Photogravure is an intaglio process, in which hardened

gelatin protects certain parts from the etching action of acid. The details are not directly concerned with photochemistry.

Colour Printing—The Three-colour Process.—Colour printing is based on the Young-Helmholtz theory of colour vision, which assumes three independent subjective sensations, each stimulated by a different set of wave-lengths of light. The three sensations present equally cause the perception of white light, separately they appear as red, green, and violet. The colour of two sensations is that given by white *minus* the third. Clerk Maxwell showed that by using three transparent coloured filters, each made so as to transmit a single sensation, three ordinary photographs could be obtained and used to re-constitute a coloured image. In printing, this is attained by a *subtractive* method, *i.e.* by using the photographs successively to subtract the reflecting power of a white surface for their respective colour sensations. The negative made with the violet filter will be transparent for all parts of the subject not reflecting violet light, these parts will deposit ink in the paper. The ink must *subtract* the reflecting power for violet, *i.e.* its colour must be white minus violet = red plus green = yellow. The red filter will require a white minus red ink = violet and green = greenish-blue ink, and the green filter will correspond with a pink ink. Three printings are made successively with yellow, pink, and greenish inks, and the impressions must exactly coincide.

Photography in Colours.—Colour photography is another product of the Young-Helmholtz theory of colour vision. The first difficulty arose from the startling discrepancy between the subjective brightness of colours and their intensity as recorded by an ordinary photographic plate.

Colour.	Luminosity to the eye.	Relative Exposures on ordinary plate.
Ultra-violet	Nil	Small
Violet	4–7	Small
Blue	7–12	Small
Blue-green, green	12–60	4
Yellow, green-yellow	60–100	36
Orange	70–80	120
Red	8	1,600
Infra-red	Nil	Very great

(Exposure for white light = 1)

The advent of panchromatic plates overcame the difficulty of *recording* yellow and red light, but still left the blue, violet, and ultra-violet rays disproportionately effective. It was accordingly necessary to introduce colour filters transmitting red and yellow, but absorbing blue and violet rays.

In order to ensure correct results, the spectral distribution of the light, the selective absorption of the filter and the spectral sensitivity of the panchromatic plate must all be determined by careful physical measurements.

A nice adjustment between the three variables is essential, and a set of filters suitable for daylight, gas-light, and filament lamps must be available. The correct tint of the filter is thus fundamentally important and spectroscopic control is imperative (for methods, see p. 271).

It would take up too much space to follow the evolution of colour photography historically. It must suffice to say that no satisfactory solution of the problem of coloured *prints* is yet available, whereas coloured transparencies have reached a very promising standard, and one or two of the successful processes may be described.

The Lumière "Autochrome" process employs a mosaic of tiny starch grains, some 7 millions to the square inch. The grains are dyed orange-red, green, and blue-violet, mixed in the ratio 3 : 4 : 2 and rolled flat on to a sticky surface. The interstices are filled in with a black pigment, and the whole plate is varnished and coated with a panchromatic emulsion. The plate is exposed with the glass side uppermost, so that the starch grains act as a close packed arrangement of tiny screens, and a special filter is used behind the lens.

The plate is very slow (H. and D. 10), and on development the image appears in complementary colours. The negative silver image is dissolved away by acid permanganate, and the plate is again developed in daylight. The result is a positive, showing the colours of the subject. Intensification is usually necessary.

Replicas may be obtained by copying or by fixing a

plate after the first development and making positives directly.

The Paget screen plate employs a mosaic of some 40,000 coloured squares to the square inch. This screen is used for taking a transparency, and another slightly different screen is used for viewing. The Paget process gives very beautiful results, but accurate registration is difficult.

Colour photography has been applied to cinema photography in various ways. The most interesting process is that of Kelley (B. J. Photography), known as the "Prizma" film. This most elegant method is too intricate to be described in detail, but its value may be realised from the fact that a single unit of film shows the complete colour effect. The film can be projected in the ordinary way without colour screens.

Two photographic processes remain to be considered, which involve a reaction rather different from those we have so far considered. One consists of the reduction of ferric to ferrous salts :

$$Fe^{\cdots} \xrightarrow{\text{light}} Fe^{\cdot\cdot} .$$

In the well-known "blue-print" process ferric hydroxide is dissolved in citric acid, and an equivalent amount of ammonium citrate is added. On exposure the ferric ion is reduced to ferrous ion, and the print is then bathed in a solution of potassium ferricyanide with resultant formation of Turnbull's blue, $Fe_3(Fe(CN)_6)_2$.

The prepared papers contain the ferricyanide and the double citrate, and the blue image is formed directly. The print is fixed by washing in very dilutic acid. If the image is developed with potassium ferrocyanide the exposed part forms colourless ferrous ferrocyanide, which is removed, and the unchanged ferric salt forms Prussian blue.

The beautiful platinotype process depends on the reduction of ferric oxalate :

$$Fe_2(C_2O_4)_3 \xrightarrow{\text{light}} 2Fe(C_2O_4)+2CO_2$$

Potassium chloroplatinite and ferric oxalate are first mixed

and coated on to the paper. The reaction which occurs follows the equation :

$$2Fe(C_2O_4)+3K_2PtCl_4 \rightarrow Fe_2Cl_6+6KCl+4CO_2+3Pt$$

The print is developed by means of a solution of potassium oxalate, which forms a soluble double ferrous oxalate, which then reacts with the chloroplatinite. The developer may be incorporated with the sensitising mixture, so that the paper is then a printing-out paper.

The platinotype process gives very permanent prints which excel in delicacy of tone. The paper is, however, expensive, and must be stored in a specially dry atmosphere.

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The *Annual Reports on the Progress of Applied Chemistry* contain a number of invaluable reports on the photographic industry.

Photography as a Scientific Implement, a collective work, published in Messrs. Blackie's "Applied Physics Series," contains important chapters, amongst which the following are especially useful to chemists :

The Theory of Photographic Processes and Methods, by S. E. Sheppard.
Colour Photography, by W. L. F. Wastell.
Photography Applied to Printing, by W. B. Hislop.

Baly's *Spectroscopy*, Vol. II, Chap. V, is concerned with the photography of the spectrum. Wedge spectra of various sensitisers are shown, together with remarkable photographs showing the effect of the latest sensitisers.

The article by Slater Price, Ref. (4), is especially valuable as a general summary of the latest investigations.

SECTION VI.—PHOTOCHEMISTRY AND LUMINESCENCE

Photo-Electricity.—When exposed to light, selenium changes its electrical resistance, a fact discovered as long ago as 1873 by Willoughby Smith.[1] Case [2] made a search for other substances sharing this property, and found that acicular crystals of bismuth trisulphide and granular lead-antimony sulphide did so to a marked extent. As a result of investigations on these lines the remarkable "Thalofide Cell" was evolved. This is a photo-electric cell in which the light-sensitive material contains thallium, oxygen, and sulphur. The resistance in the dark is about twice as great as that observed when the cell is illuminated by a heated tungsten filament ($\frac{1}{16}$–$\frac{1}{4}$ foot-candle). The cell is sensitive to infra-red rays.

The mechanism of the change in resistance of selenium presents a difficult problem. Berndt [3] and Marc [4] consider that the light effects transformations between selenium allotropes, but the fact that no heat evolution can be observed militates somewhat strongly against this view. The persistence of the light-sensitivity at a temperature as low as that of liquid air on the contrary supports the view of Ries [5] that slow-moving electrons are set free, but fail to escape from the mass of substance, and by remaining diminish the resistance.

It has been shown by Kolzareff [6] and Geiger [7] that molybdenite, argentite, and other minerals develop an electromotive force of the order of 0·01 volt under strong illumination.

When illuminated by ultra-violet light a negatively charged plate of bright metal gives off electrons.

When the illuminated area forms one plate of an air condenser, the other plate being positively charged from a battery, it is possible by using a sensitive galvanometer or a quadrant electrometer to measure the current produced.

In the case of the alkali metals, it was shown by Elster and Geitel[8] that visible light produced the same effect, rubidium giving off electrons under the influence of a glass rod heated just to redness. Freshly polished surfaces of zinc and aluminium show the photo-electric effect when exposed to sunlight.

Lenard, Elster and Geitel, Millikan, and many other workers have contributed to establishing the following facts :

(*a*) The *velocity* of the electrons is independent of the intensity of the light.

(*b*) The *number* of electrons emitted is directly proportional to the intensity of the light.

(*c*) For every surface there exists a minimum (threshhold) frequency ν_0 below which emission of electrons cannot occur.

(*d*) Beyond this point the velocity of the liberated electron increases continuously as the frequency of the (monochromatic) light increases.

(*e*) The photo-electric effect may vary with the polarisation of the light, *e.g.* in the case of a liquid alloy of sodium and potassium Elster and Geitel found that when polarised white light fell upon the surface at an angle of 45° the current reached a maximum when the electric vector in the light wave was vibrating in the plane of incidence, and when the electric vector and the plane of incidence were at right angles the current reached a minimum value.

Einstein, using the idea of " quanta," suggested the relation :

$$\tfrac{1}{2}mv^2 = Ve = h\nu - h\nu_0$$

h = Planck's constant,
ν = frequency absorbed,
ν_0 = threshold frequency,
V = voltage necessary to retard the velocity to zero,
e = electronic charge,
$\tfrac{1}{2}mv^2$ = energy with which the electron is liberated.

The validity of this equation has been proved by Millikan [9] and used as a basis for the determination of $h(6{\cdot}554 \times 10^{-27})$.

The study of the effect of polarised light has led to a sharp discrimination between what are called the *normal* and *selective* photo-electric effects.

In both the maximum velocity with which electrons are emitted is independent of the orientation of the plane of polarisation. For the normal photo-electric effect, the number of electrons set free depends only on the polarisation to the extent that the light-absorption does, whereas in the selective effect the number of electrons liberated is much greater when the electric vector vibrates in the plane of incidence. In the selective effect, a maximal number of electrons is emitted for a particular frequency.

Little is known concerning the relation between photo-electric and chemical properties.

Allen [10] found that chemically active iron was much more effective in the photo-electric sense than passive iron. Frese [11] observed that whilst reducing agents like nascent hydrogen increased the photo-electric sensitivity of a metal, oxidising agents acted in the opposite sense.

The experience of many workers goes to show that the more electro-positive a metal, the greater is its photo-electric activity (the tests being made in air).

Among the chemical compounds investigated the sulphides and some halides stand out as markedly sensitive. Cuprous and chromous sulphides as well as bismuth trisulphide show large effects. Silver halides are similarly sensitive,[12] but the alkali halides are inactive.

A considerable body of information is available on the

photo-electric sensitivity of inorganic compounds, but it is very difficult to interpret (see Allen's *Photo-electricity*).

In order to illustrate the present state of knowledge in regard to the effect with organic compounds, perhaps the best way is to record a few of the facts and leave the problem of interpretation on one side.

Hydroquinone is active, resorcinol is inactive. Fuchsin and methyl violet are both sensitive, but the electron emission differs enormously in the two cases.

The following are active : Eosin, fluorescein, malachite green, magdala red, aniline green, aniline violet, cyanin, iodine green, many benzene derivatives. In the latter case it has been argued by Stark that for certain absorption bands, absorption results in both photo-electric effect and fluorescence.

It would be interesting to know how many "photochemical" reactions are really secondary changes following a photo-electric action.

The advent of photo-electric cells has been of great practical advantage in the measurement of light intensity. The instrument is so sensitive that satisfactory response may be obtained with energies as low as 10^{-7}–10^{-8} erg/sec. cm.^{2}, the photo-electric current being then of the order 10^{-15} ampere. Valve amplification is, of course, very useful in work of this type. The most usual metal is potassium either as free metal or hydride, and the General Electric Company now manufacture photo-electric cells containing alkali metal in the untreated state. The cells exhibit no time lag, and they are also free from photo-electric fatigue. Potassium cells show a maximum sensitivity near 441$\mu\mu$. Szilard describes a cadmium cell sensitive to rays in the region 295–390$\mu\mu$, which is claimed to be specially suitable as an ultra-violet actinometer. The quartz-cadmium cell has been developed by Griffith and Taylor [13, 14], who have shown it to provide a satisfactory means of comparing the abiotic or bactericidal action (see p. 195) of quartz-mercury lamps of widely differing types.

As illustrations of the practical value of photo-electric

photometry, we may instance researches carried out at the U.S. Bureau of Standards on absorption spectra, and the work of von Halban and his collaborators on the same subject, with particular reference to the validity of Beer's Law.

A recent paper by Griffith and Jack [15] on "The Efficiency of Carbon Arcs as Sources of Ultra-violet Light" provides an example of a practical problem in which the cadmium cell was found useful.

Photo-electric cells have found an important practical application in the "Phonofilm." A cinematograph camera of the usual type is fitted with a small discharge tube known as the Photion lamp, adjusted so that a thin strip of film is exposed to a beam of light of constant intensity. The lamp is connected to a microphone wireless circuit, so that when the music or speech commences the sound variation will be transformed into flickerings of the lamp. The film is wound mechanically and the ordinary cinema negative is, of course, made simultaneously.

For reproduction, a fine beam of light strikes the sound record on the film and variations in emergent light intensity cause variations in photo-electric current, using special de Forest cells. The rest of the work is a matter of wireless technique, valve amplification, loud speakers, etc.

In preparing the negative the film has necessarily to move in jerks through the camera, but the sound record must be continuous. For this reason the discharge tube is fixed between the lens and the top film spool, so that there is about nine inches between the sound record and its accompanying picture. The photographic record is therefore advanced nine inches in preparing the positive, so as to secure synchronisation.

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Photo-voltaic Cells.—Becquerel[1] observed that when he placed silver or platinum electrodes coated with silver halide in a dilute solution of sulphuric acid, a potential difference was set up between the two electrodes if one was exposed to light and the other kept in the dark. The sign of the charge on the illuminated electrode depended on the thickness of the layer of light-sensitive material, whilst the voltage varied with the intensity of the light. A platinum electrode coated with silver halide acted as cathode when exposed to light, the cell solution being dilute sulphuric acid. On the other hand, a cell made up with the same acid and containing silver electrodes coated with silver halide behaved as follows: If the layer of halide was thick and uniform the illuminated plate acted as anode, whilst if the electrode was only thinly coated it acted as cathode.

Minchin[2] set up the following cells:

Exposed to light.	Ag | AgCl	NaCl	AgCl | Ag
Cathode		$\longleftarrow$	
Exposed to light.	Ag | AgBr	KBr	AgBr | Ag
Cathode		$\longleftarrow$	
Exposed to light.	Ag | AgI	$AgNO_3$	AgI | Ag
Anode		$\longrightarrow$	Cathode

As a result of Minchin's work, it was established that the photo-voltaic effects were dependent on the nature of the photo-sensitive material, the thickness of the layer used, and the nature of the cell solution. It was also found that in many cells the direction of the current was reversed after a brief period.

Wildermann[3] took up the investigation of the subject, and some of his results may be tabulated:

Cathode exposed to light. ←		Cell solution.	Anode.	
Metal.	Thin layer sensitive material.		Thin layer sensitive material.	Metal.
Ag	AgCl	N/10NaCl	AgCl	Ag
Ag	AgBr	N/10NaBr	AgBr	Ag
Ag	AgBr	N/10KBr	AgBr	Ag
Ag	AgI	N/10KI	AgI	Ag
Hg	Hg_2SO_3	N/10K_2SO_4	Hg_2SO_4	Hg
Cu	CuO	N/40NaOH	CuO	Cu

Case[4] set up the cell:

Anode, exposed to light.	2·5 per cent. Copper formate →	Cathode
Cu′ | CuO (Thick even layer.)	0·4 per cent. Formic acid	CuO′ | Cu

With this cell a very interesting result was obtained, since by closing the external circuit an electromotive force of 0·11 volt was set up and a current flowed away from the illuminated plate. Upon continued exposure to light the current gradually fell to zero, but if the dark and illuminated electrodes were reversed the current immediately regained its initial value. The photo-sensitive material thus seems to undergo gradual destruction at the illuminated surface but to be reformed at the darkened surface.

Garrison[5] was able to confirm the reversal effect first noted by Minchin, and obtained the following results:

Exposed to light.		
Cu′ | Cu_2O	K_2SO_4 ←	CuO′ | Cu
(Thin layer) Cathode		(Thin layer) Anode
Exposed to light.		
Cu′ | Cu_2O	K_2SO_4 →	Cu_2O | Cu
(Thick layer) Anode		(Thick layer) Cathode

With medium layers the polarity seemed to depend on the

nature of the cell electrolyte, since addition of sulphuric acid reversed the anode tendency, whilst addition of potassium hydroxide increased the original anode tendency.

Tucker[7] has recently made a thorough theoretical and experimental study of the problem, and has arrived at the following general rules :

(1) In a photo-voltaic cell, with two electrodes consisting of a photo-sensitive substance on platinum and dipping into an oxidising solution, illumination will cause the exposed electrode to behave as a cathode, if the photo-sensitive substance present is tending to be photochemically oxidised when illuminated in contact with the same oxidising solution.

If this same electrode system is dipped into a reducing solution, the illuminated electrode will behave as an anode, if the photo-sensitive substance is tending to be photochemically reduced when illuminated in contact with the reducing solution.

(2) In a photo-voltaic cell with electrodes consisting of the same metal from which the metallic constituent of the photo-sensitive material is derived, illumination tends to produce a photochemical reduction of the photo-sensitive substance.

(3) If the photo-sensitive substance is on the illuminated electrode as a uniform layer, local cell formation on the illuminated surface will be at a minimum and the exposed electrode will be an anode.

(4) If the photo-sensitive substance is on the illuminated electrode as a non-uniform layer, local cells will be set up in the illuminated electrode. If these local cells tend to polarise, the illuminated electrode will eventually become a cathode after continued illumination. If these local cells do not polarise but are completely reversible, the electrical behaviour of the illuminated electrode will be determined by the oxidising or reducing nature of the cell solution. In an oxidising solution or a neutral solution the illuminated electrode will be a cathode, while in a reducing solution the illuminated electrode will be an anode. If these local cells

approach towards, but do not attain complete reversibility, the illuminated electrode will be cathode in oxidising or neutral solutions and may or may not be cathode in reducing solutions.

These rules suffice to account for the observations made by Tucker himself and also to reconcile the results of the earlier workers.

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Phosphorescence.—The simplest view of phosphorescence is to regard the phenomenon as the emission of " cold " light. This very unscientific expression implies that we usually experience the sensation of heat when we perceive light, and that the absence or comparative absence of heat is unusual. The emission of energy in the form of light is indeed in most cases necessarily associated with high temperatures, and of the total energy used in a source of light the major portion is radiated away thermally and only a small portion as visible radiation. A system is described as " luminescent " when the radiation emitted is greater in amount than that which can be traced to the temperature (*i.e.* black body radiation). Luminescence is a very general effect. It may be observed with substances in the gaseous, liquid, or solid states, and as a rule the wave-lengths of the light emitted are characteristic of the chemical composition of the substance subjected to excitation. The exciting agency may be light (photo-luminescence), friction (tribo-luminescence), cathode rays (cathodo-luminescence), electrical (electro-luminescence, and a special case in Tesla-luminescence where the Tesla coil discharge is used). Thermo-luminescence is defined as the development of a *characteristic* emission of light when certain solid materials are heated.

Photo-luminescence includes two separate phenomena—fluorescence and phosphorescence. In some cases the luminosity vanishes the instant the exciting light is cut off. This phenomenon is called fluorescence, and a good example is the blue fluorescence of quinine bisulphate under the action of ultra-violet rays. In other cases the luminescence continues for a finite period of time after the exciting light has been cut off. The persistence of the luminosity varies widely in different preparations, and the measurement of its duration has thrown much light on the phenomena of phosphorescence. The best known example is in the luminous paints containing impure sulphides of calcium or barium. These paints glow in the dark after exposure to sunlight, and show a persistence of long duration.

All substances can absorb and radiate energy, and very frequently some wave-lengths play a predominant part in the phenomena; in other words, selective absorption and emission occur. It is possible for a material to take in energy in the form of cathode rays, X-rays, or light, and to give it out again in another region of the spectrum. In fluorescence the process may be regarded as simply one of exchange—or transformation of energy. In phosphorescence the excited body actually *stores* the energy for a greater or less period of time.

In gases it may happen that molecules *absorb* light of a definite wave-length and *emit* exactly the same wave-length, a phenomenon known as optical resonance. Stokes showed that fluorescence and phosphorescence always occur at wave-lengths longer than those which excite them. This generalisation is known as Stokes' law, and is regarded as fully established. Fluorescence occurs with many organic compounds in solution, *e.g.* eosin, fluorescein, etc., but phosphorescence has only been observed with substances in the solid state.

Crystalline structure appears to be essential, although this condition possesses little meaning now that X-ray studies have demonstrated the extreme rarity of the amorphous state.

Phosphorescence may be further defined as follows: a phosphorescent body can exist (*a*) in its normal state, (*b*) in the state in which it is giving out light, the time occupied in converting it from the (*a*) to the (*b*) condition being less than the time occupied in the reversion from (*b*) to (*a*), *i.e.* in the emission of light. This simply means that in the process of phosphorescence energy must be temporarily stored. The intensity of phosphorescence is greatly affected by concentration and by temperature. As has already been stated, excitation may occur by means of cathode rays, X-rays, or light. In the latter case it is easy to study the effect of using either heterogeneous light or monochromatic light. Preparations of phosphorescent materials are called *phosphors*, and in most cases they consist of solid solutions. The fundamental magnitude characteristic of a phosphor is its *persistence*, or, alternatively, the *rate of decay* of the intensity after excitation has ceased. The persistence depends on the concentration of the active principle and on the temperature.

The classical investigation on phosphorescence is that of Lenard and Klatt [1] on the alkaline earth sulphide phosphors. These authors found that:

(*a*) *Pure* barium sulphide, calcium sulphide, and strontium sulphide do not phosphoresce.

(*b*) A phosphor must contain (1) the sulphide, (2) a trace of an "active" metal, (3) a flux.

(*c*) Easily fusible salts mixed with an alkali sulphide do not give phosphorescent mixtures in the absence of impurities.

(*d*) The colour of the phosphorescence is determined primarily by (1) and (2), but only very secondarily by (3).

(*e*) The quantity of active metal present in a good phosphor is exceedingly small.

(*f*) Phosphors cannot be produced in the wet way: the mixture must be heated to redness.

(*g*) The phosphors lose their activity under pressure or other mechanical stress. This means that a

mixture should be left in a friable condition after the heating process, and that fusion should therefore be avoided.

In a series of investigations, Lenard and Klatt showed further that the light emitted by a phosphor containing one active metal consists of numerous bands of different wave-lengths. The flux used determined the relative intensities of the different bands, so that the visible colour of the light emitted might be changed by changing the flux, although the wave-lengths of maximum emission would not be altered.

A simple nomenclature has been devised for phosphors, *e.g.* CaSBiNa stands for a phosphor containing calcium sulphide with a trace of bismuth as the active metal, and a sodium salt as the flux :

Diluent.	Luminogen.	Emission band.	Excitation band.	Fusible component.
CaS	Bi	*a*	d	Na_2BO_4

The metals known to be active are copper, bismuth, manganese, silver, zinc, lead, antimony, nickel, and some rare earth metals.

Preparation of Phosphors.—Phosphors are exceedingly sensitive to the presence of impurities, a concentration of one in a million of copper, for instance, may be detected with great ease. Hence, if it is desired to repeat the preparation of an accurately described phosphor, great purity is essential. Conversely many recipes are valueless because of the presence of impurities in the ingredients used originally.

The first step is the production of pure alkali earth sulphides. In the case of calcium the reaction

$$4CaO + 4S \rightarrow 3CaS + CaSO_4$$

occurs on heating.

Owing to volatilisation the amount of sulphur used is somewhat greater than is indicated by the stoichiometric equation, and the best preparations are obtained with the ratio CaO : S = 2 : 1·35.

The heating operations are carried out in platinum-lined crucibles. The calcium sulphate is inert and merely acts as a diluent. If this sulphide preparation is heated with a flux the resultant material usually phosphoresces slightly, owing to the presence of a minute trace of copper; but this residual phosphorescence is masked by the new effect which occurs when another metal is added.

In the preparation of phosphors the active metal is added in the form of an aqueous solution of the nitrate, except in the case of antimony, when the tartrate is used.

Solutions [2] of known concentration are used and a measured quantity is employed in each case. Weighed quantities of the sulphide and flux are mixed together and then spread out over the bottom of the dish, a small cavity is made in the surface by means of the pestle, and the cavity is filled with ten to fifteen drops of absolute alcohol, the necessary number of drops of the metallic salt solution being added last. The whole is gently ground up so as to secure equal distribution of the metallic sulphide throughout the whole. The mixture is then placed in a platinum-lined porcelain crucible and heated at a bright red heat in a Hempel oven, usually for twelve to twenty minutes. The importance of the type of heat treatment will be dealt with below.

The following may be given as typical calcium preparations:

CaCuNa. 3 grm. Sulphide, 0·2 grm. Na_2SO_4, 0·77 grm. NaF, 0·002 grm. Cu.

CaCuLi. 3 grm. Sulphide, 0·2 grm. Li_2SO_4, 0·07 grm. CaF_2, 0·002 grm. Cu.

CaCuK. 2 grm. Sulphide, 0·15 grm. K_2SO_4, 0·0013 grm. Cu.

CaPbK. 2 grm. Sulphide, 0·12 grm. K_2SO_4, 0·1 grm. CaF_2, 0·0017 grm. Pb.

CaPbNa. 3 grm. Sulphide, 0·15 grm. Na_2SO_4, 0·08 grm. NaF, 0·00084 grm. Pb.

CaMnNa. 2 grm. Sulphide, 0·1 grm. Na_2SO_4, 0·05 grm. CaF_2, 0·00093 grm. Mn.

CaNiF. 4 grm. Sulphide, 0·3 CaF_2, 0·00006 grm. Ni;

heated for 10 minutes, then ground up with more sulphur and again heated for 30 minutes at the highest temperature of the Hempel oven.

CaBiNa. 2 grm. Sulphide, 0·1 grm. Na_2SO_4, 0·05 grm. $Na_2B_4O_7$, 0·05 grm. CaF_2, 0·0048 grm. Bi.

CaSbNa. 3 grm. Sulphide, 0·15 grm. Na_2SO_4, 0·06 grm. NaF, 0·0013 grm. Sb.

In the case of strontium phosphors the sulphide is prepared by moderately heating an intimate mixture of 5 grams $SrCO_3$ and 2 grams of powdered crystalline sulphur. Mixtures of this sulphide with the various fluxes after heating show evidences of copper phosphorescence, but, as in the case of calcium, this is masked in the phosphors prepared from it. The following phosphors may be mentioned, the quantities being expressed in grams :

SrCuNa. 4 Sulphide, 0·1 Na_2SO_4, 0·1 $Na_2B_4O_7$, 0·00018 Cu.

SrPbLi. 2 Sulphide, 0·3 Li_3PO_4, 0·02 CaF_2, 0·00014 Pb.

SrAgNa. 2 Sulphide, 0·06 Na_2SO_4, 0·00016 Ag, not too strongly heated.

SrZnF. 3 Sulphide, 0·1 CaF_2, 0·0005 Zn, moderately heated for 3 to 4 minutes, then ground up with some sulphur and heated moderately strongly for 12 minutes.

SrMnNa. 3 Sulphide, 0·1 Na_2SO_4, 0·00005 Mn.

SrBiNa. 3 Sulphide, 0·1 Na_2SO_4, 0·00024 Bi.

The preparation of barium sulphide is complicated by the tendency to form polysulphides, which colour the product yellow and depreciate the phosphorescence. These may, it is true, be destroyed by prolonged heating, but this is unsatisfactory. If 10 grams $BaCO_3$ are heated with 2·25 grams of sulphur the maximum yield of sulphide is obtained, and the colour is practically white, but a longer period of heating is necessary than in the cases of calcium and strontium. The presence of copper is again indicated by its phosphorescence, but, as before, this has no deleterious effect. As typical phosphors the following may be given :

BaCuNa. 3 Sulphide, 0·03 NaF, 0·00024 Cu.
BaPbNa. 3 Sulphide, 0·1 Na_2SO_4, 0·00028 Pb.
BaBiK. 3 Sulphide, 0·1 $K_2B_6O_{10}$, 0·00024 Bi.

Brief reference was made above to the effect of varying the temperature and time of the heat treatment. In general these have the greatest influence on the total intensity of the phosphorescence, that is to say, all the bands of each metal are equally influenced. To obtain the best results, that is, the fullest development of the emission bands, it is advisable to heat the mixtures at a sufficiently high temperature and for sufficiently long, so that the binding effect of the flux can be exerted to its fullest extent, and thus prevent as much as possible the oxidation of the sulphides. In some cases the relative intensities of the emission bands of a metal are affected to a remarkable extent by changes in the heat treatment. This is well exemplified by SrAgNa and SrAgLi phosphors, which with a slow heat treatment give a reddish phosphorescence, whilst with longer and stronger heating the colour becomes more and more violet. This is due to a relative increase in the intensity of the violet band caused by the increased time and temperature, the nature of the flux being of far less importance.

We may now turn to the results obtained by Lenard and Klatt in their investigation of the many phosphors prepared by them. In the first place, the effect of varying the flux may be mentioned, and the following general conclusions may be given. In the case of some active metals, such as zinc, bismuth, and manganese, the nature of the flux has little effect on the colour of the phosphorescence, that is to say, the relative intensities of the bands of each metal are not influenced by the flux. On the other hand, with some active metals, such as copper and lead, the colour of the phosphorescence is very materially affected by a change in the flux, it being possible by varying the flux to obtain two or more colours. Here it is found that salts which are chemically similar have the same effect, this being shown in two different ways. Amongst the salts of the oxygen containing acids it is the metal which has the predominating influence. Thus all the sodium salts have the same influence, and so on. The opposite is true with

the halides, since it is the halogen element which has the dominating influence, and all the chlorides and all the fluorides having their own specific effects. These relationships are especially exhibited with the calcium sulphide phosphors; in the strontium sulphide and barium sulphide phosphors the various fluxes fall into groups with similar effects, but in these cases the grouping is not so obviously based on chemical analogies.

As has been stated, phosphorescence may be excited by cathode rays as well as by light. An outstanding paper in this field is due to Urbain and Bruninghaus.[3] We cannot enter into the details of this work, but some account of the very precise views of the authors must now be given.

(1) A pure substance will not phosphoresce.

(2) The degree of purity necessary to eliminate phosphorescence is very high and is often very difficult of realisation. Phosphorescence is thus only shown by a mixture of at least two substances.

(3) A substance does not become phosphorescent until it contains in solid solution a trace of a heavy metal, *e.g.* copper, bismuth, manganese, or some of the rare earths. Phosphorescence is thus a property of diluted matter, the diluent being usually a sulphide or an oxide and the *luminogen* or *phosphorogen* a heavy metal.

(4) The concentration of the luminogen must be very small (of the order 1 in 10,000) or else the luminescence ceases. Urbain calls this the law of optimum, since it is applicable to all phosphors.

(5) The spectrum of the phosphorescent light consists usually of diffuse bands. The nature of the luminescence is determined primarily by the phosphorogen and only secondly by the diluent. Phosphorescence can only occur within a limited range of temperatures, so that optimum conditions of brightness or duration can only be obtained after taking the temperature effect into account.

These conclusions are qualified by the work of Nichols

and his colleagues (see Baly, p. 316; *Spectroscopy* (1927), Vol. II, Longmans).

Urbain has applied the cathode ray phosphorescence to the difficult task of controlling the separation of rare earths. At certain stages in the process of recrystallisation fractions may be obtained which do not appear to change in composition with further fractionation. Such fractions may be pure salts of a single metal or may be mixtures of constant composition; in the latter the fraction will probably phosphoresce strongly, whereas the absence of phosphorescence is a good indication of a single pure compound.

A word of warning is necessary against the too literal acceptance of the dictum that *all* pure compounds do not phosphoresce. Levy[4] prepared three markedly different modifications of barium platinocyanide, two crystalline and one amorphous, all apparently pure.

	Crystalline A.	Crystalline B.	Amorphous.
Colour	Orange	Apple-green	Brick-red
Crystalline form ..	Identical	Identical	None
Fluorescence ..	Very feeble	Very brilliant	None

The green salt fluoresces fifty times as strongly as the orange salt.

Progress in the study of luminescence is, of course, bound up with theoretical interpretation—in this instance a very difficult task. On the basis of the Bohr theory of the atom, emission may be said to occur when an electron approaches the centre of attraction of the grouping of which it forms a part, and we have the well-known mechanism of quantum jumps and stationary states. The absorption of a quantum of the exciting radiation raises the electron to a higher energy level, from which it may fall to the accompaniment of light emission. The Bohr theory readily allows the emission of *monochromatic* phosphorescence, but it fails to give a complete picture of the whole process. The limiting case of an electron displacement is the photo-electric effect. Einstein's photo-electric equation

$$h\nu = W + \tfrac{1}{2}mv^2$$

gives the kinetic energy of the liberated electron, and it

follows that the frequency of the exciting radiation must be greater than W/h. Lenard has developed a theory of phosphorescence based on this photo-electric effect. An electron is set free by the exciting light and in its return it gives rise to the luminescence phenomenon. Three possibilities exist:

(*a*) The electron is completely detached.

(*b*) The electron fixes itself on an outer orbit, the atom or molecule remaining in an excited Bohr state.

(*c*) The liberated electron attaches itself to an outer orbit in a neighbouring atom or molecule.

These possibilities make Stokes' law inevitable, and they provide excellent guidance for unravelling the maze of observations.

The latest contribution to the theory of phosphorescence is that of Baly (*Spectroscopy* (1927), Vol. II, Chap. IV).

He pictures a molecule as capable of existing in two *molecular phases.*

A		B
Can absorb light of frequency ν.	Absorbing energy. →	Becoming activated.
Exists on low energy level normal state.		Exists on high energy level of greater energy content.
A	← Radiating energy.	B

A striking argument for the reality of these molecular phases differing in respect of energy content is given by Baly's observations on fused quartz, which he has kindly allowed the author to quote in full.

"It is well known that fused silica in layers of about 2 mm. thick is markedly transparent to ultra-violet light to as far as the wave-length 1900 Å. If this material is exposed to the radiation from a quartz-mercury lamp for some days, then, provided it is kept cool, the silica develops an amethyst colour exactly similar to that of natural amethyst quartz. Not only has the silica now developed a visible colour, but it has also become opaque to ultra-violet light of short wave-length. This new condition of the silica is metastable, and if it is heated to about 500°, or if it is crushed,

it emits a brilliant green phosphorescence and returns to its normal colourless state which is transparent to short-wave ultra-violet light. In this we find conclusive evidence of the existence of fused silica in two different states, a colourless state transparent to short-wave ultra-violet light, and a coloured state opaque to short-wave ultra-violet light. We have, too, conclusive evidence that the coloured state has the higher energy content, since, apart from the fact that it is produced from the colourless state by the absorption of light energy, we have the incontrovertible fact that in passing to the colourless state radiant energy is visibly emitted. Perhaps a word of explanation is advisable on the question of the production of the coloured state by the absorption of light energy by the colourless state. It must be remembered that although the colourless state is markedly transparent to the short-wave ultra-violet light, it possesses a definite and measurable absorptive power towards that light. Since it is this light only which effects the change it may be accepted without hesitation that the change is due to the fraction of that light which is absorbed."

Baly's next step depends on important observations carried out by Schmieder on the quantitative relations between absorption and luminescence. Schmieder [5] proved that for every quantum of exciting light absorbed one quantum of energy was emitted as luminescence.

By Stokes' law the exciting quantum must be greater than the emitted quantum, and the difference was shown to be emitted as infra-red radiation, *i.e.*

$$h\nu_1 = h\nu_2 + x$$

Exciting quantum = Emitted quantum + Thermal radiation

Now to return the equation A→B (see above) the activated phase may be, (*a*) quite unstable when the luminescence would be expected to be instantaneous, (*b*) metastable when the emission might occur more slowly. If the phase A is characterised by absorbing a quantum of size $h\nu_1$, and B by radiating a quantum $h\nu_2$, the *nett* energy used in going from A to B is x. Baly regards this as tantamount

to saying that the difference in energy content between the energised and normal phases is x ergs.

If we now return to the equation proposed by Schmieder, namely:

$$h\nu_1 = h\nu_2 + x \text{ ergs}$$

we may re-write it in the more general form:

$$h\nu_1 = M + N \text{ ergs}$$

in which N is the difference in energy content between the phases A and B. In fluorescence (luminescence having no appreciable persistence) A goes to B by absorbing $h\nu_1$ ergs and promptly emits $h\nu_2$ ergs at the fluorescence frequency, remaining activated for a finite time, at the end of which it has emitted x ergs in the infra-red. This means that $h\nu_2 = M$ and not N.

In phosphorescence (luminescence having a definite persistence) A goes to B by absorbing $h\nu_1$ ergs and promptly emits x ergs in the infra-red, remaining activated for a finite period, at the end of which it has emitted $h\nu_2$ ergs at the luminescence frequency. This corresponds with $h\nu_2 = N$.

If neither M nor N is equal to $h\nu_2$ the whole of the absorbed quantum $h\nu_1$ is radiated in the infra-red, and there is no luminescence in the ordinary sense. This is the condition which most frequently obtains when substances absorb energy. This brief account by no means does justice to Baly's treatment, which should be consulted in the original.

Applications of Sulphide Phosphors.—The number of phosphors which have found industrial application remains small. This is probably due to the formidable demands which must be satisfied by a serviceable preparation. The phosphorescence must be in the visible and preferably at a region of the spectrum close to the position of maximum sensitivity of the eye. It must be excited by blue, violet, or near ultra-violet rays, and it must combine some measure of persistence with an appreciable intensity.

Phosphors have been proposed for stairs, commutators, switches, bell-buttons, keyholes, fire-alarms, fishing-tackle, compasses, aeroplanes, and dark-room clocks, etc.

The greatest disadvantage is the lack of intensity. Quite good phosphors rapidly become very faint, as is shown in the table.

Time after cessation of excitation.	Phosphor ZnSCu.	CaSBi.
10 Secs.	225	25·4
30 Secs.	57	8·5
1 Minute	36	6·0
10 Minutes	3·5	0·77
30 Minutes	0·85	0·25
1 Hour	0·35	0·11
2 Hours	0·14	0·055
3 Hours	0·04	0·02

The units are millionths of a candle-power per square cm. The luminosity can be perceived at the end of several hours, but *only in complete darkness.*

It has been said that after a few hours the light from the most powerful phosphors scarcely exceeds that of a piece of white paper receiving the " obscure clearness of the light from the stars."

Certain substances become luminescent when exposed to bombardment by α-particles from radium, *e.g.* zinc sulphide (yellowish-green), calcium tungstate (blue-green), calcium phosphate (red), willemite (green), calcium sulphide (green). X-rays and ultra-violet rays also cause some of these compounds to luminesce, but no simple connection between the actions of α-particles and short-wave radiation has yet been demonstrated. Yet there is a decided resemblance between the phenomena, since in both, very pure compounds do not become luminescent with the same ease as when a trace of impurity is present. Both for α-particle excitation and ultra-violet or X-ray excitation the intensity and colour of the luminescence vary as the impurity is changed. Sidot's hexagonal zinc-blende, of all the substances tried, gives the greatest intensity of light when exposed to the action of radium. Methods devised by Glew for the preparation of zinc sulphide luminous compounds are quoted in the *Dictionary of Applied Physics* (Vol. IV, p. 195, Macmillan, 1923). There are two ways of mixing the zinc sulphide and radium. (*a*) Dry method, involving careful mixing in an agate mortar without crushing the

zinc-blende crystals. (*b*) Wet method, involving the use of a known quantity of a soluble radium salt treated with a known volume of distilled water containing a trace of hydrochloric acid. A calculated volume of solution is placed in a porcelain dish and zinc sulphide is added until all the liquid is absorbed. The mixture is now dried on a water-bath and stirred to prevent caking. In removing and powdering the mass, care should be taken not to exert great pressure at any point.

To apply the luminous preparation to a surface a small heap of powder is placed on a watch-glass and a few drops of turpentine, followed by a small amount of varnish, are added. When the luminous paint is to be used on silver, brass, copper, or iron, the surface must first be treated with zinc-white and varnish (white-lead should not be used, as the black lead sulphide reduces the luminosity of the preparation). The intensity of the glow reaches a more or less steady maximum about a week after the final coat of varnish has been laid on, but thereafter falls off slowly, owing to a deterioration in the zinc sulphide crystals.

Owen states that the initial brightness is approximately in the direct ratio of the radium content, but the preparations of low radium content exhibit a slower rate of decay than those rich in radium. "Hence, if a compound is to be used for a long period of time, there is very little advantage to be gained, except from the point of view of initial brightness, by increasing the radium content beyond a certain value."

For short-period use, say 3–4 months, the radium content may usefully be as high as 0·2 mg. of radium element per gram of compound. If the compound is likely to be required for more than six months, the use of a compound containing more than 0·1 mg. of radium element per gram of compound can *only* be justified by the need of greater brilliancy during the early part of the life.

To obtain maximum luminosity it is unnecessary to employ a thickness greater than about 0·3 mm. of a com-

pound containing 0·15 mg. radium element per gram when it is to be used over a long period of time. For the application of luminous paint to dials, see Glew (*Opt. Soc. Trans.*, 1916, **16**, 276). The best results were obtained by using 1 gram of a preparation containing 0·2 mg. per gram to cover an area of about 30 square cm. The cause of luminescence in zinc sulphide is probably connected with the occurrence of active centres, due to the presence of impurity in the zinc-blende (see *Proc. Roy. Soc.*, 1910, **84**A, 548–561; 1917, **93**A, 550).

Uses.—In aeroplanes the need for high luminosity has justified the use of paints rich in radium, and consequently of short effective life. Less luminous but longer-lasting preparations are used for wrist watches, compasses, bell-pushes, etc.

During the war much use was made of luminous radium preparations for gun sights. Small flat tubes, and in the case of heavy artillery the cross wires of the telescopic sights, were illuminated by tubes bent into a circular form and placed near the plane of the cross wires.

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Spectroscopy, by E. C. C. Baly (Longmans, Green and Co.), vol. ii, chap. iv, gives the best general account of phosphorescence from the scientific standpoint.

Commercial Production of Radium.—Pure radium chloride was first prepared in 1902 by M. and Madame Curie from pitchblende residues.

The uranium supply of the world then came from Joachimstahl in Bohemia, and in the working up of pitchblende for uranium, considerable quantities of residues had accumulated. These residues were the first important source of radium. Owing to legislation which was introduced by the Austrian Government owning the Joachimstahl mine, the mineral could not be exported. The desire to establish

an Austrian monopoly in the manufacture of radium, at once stimulated a more intense search for radiferous minerals in other countries.

An active carnotite was found in a rather inaccessible part of the United States in Colorado and Utah. Although the ore was not very rich in radium, by 1912 1,200 tons of carnotite containing 8–9 grams of radium were exported to France.

American chemists then began to work up the carnotite themselves.

RADIUM PRODUCTION FROM AMERICAN CARNOTITE

	In France.	In America.
1912	8–9 grams	—
1913	7–8 ,,	10·5
1914	7–8 ,,	22·4

A little before the war the American Government succumbed to the temptation to try to establish a monopoly. It acquired control over the industry and entered into agreements with the chemical firms concerned in the extraction of the radium.

American carnotite is not very difficult to work, although 400 tons are required to produce 1 gram of radium. The mineral consists largely of uranium and potassium vanadates, $2U_2O_3.V_2O_5.K_2O.3H_2O$, mixed with sand. It contains on an average 3·5 per cent. of vanadium pentoxide and 1·5–2·8 per cent. of uranium oxide.

For some years the American monopoly proved highly successful, but it was destined to be effectively destroyed. Very rich veins of pitchblende were discovered in the Belgian Congo, and in 1921 the Belgian Mining Society (Union Miniere du Haut Congo) began to export the ore. The extraction of the radium was carried out from 1922 onwards at Oolen, near Antwerp, and progress was so rapid that some 36 grams were produced in 1923.

On the one hand carnotite containing 0·75–2 per cent. of uranium oxide was being treated in America, and on the other the Congo ore, containing up to 60 per cent. of uranium oxide, was being worked up in Belgium. The costs of

production were entirely in favour of the Belgians, and the American works were forced to close down.

The Antwerp works has now the power to produce more radium than can be sold at the present price-level.

The Joachimstahl mine yielded up to 1922 23 grams of radium. Carnotite has yielded 160–165 grams, whilst up to 1925 over 110 grams of radium had been extracted by the Belgians. In 1924 the weight of radium sold was little over 22 grams. Probably the total production of radium has yet to reach 400 grams.

PRICE VARIATIONS OF RADIUM

	£ per milligram.
1904	2–5
1905	5–10
1911–12	31–51
1912–14	37–50
1915	30–32
1916–1922	21–25
1923	15

The extraction of radium is accomplished by the methods first used by Mme Curie and Debierne.

The extraction of uranium from pitchblende is as follows. Fusion of the finely powdered ore with sodium sulphate results in the formation of sodium uranate, which is soluble in dilute sulphuric acid. Any radium present in the ore is converted into the insoluble sulphate, and is thus accumulated in the residues.

The preliminary testing of a radio-active mineral is carried out by means of an X-ray electroscope. Carnotite is separated from sand by dissolution in hydrochloric acid. Addition of sulphuric acid brings about precipitation of barium sulphate, which carries down with it all the radium sulphate. If barium does not occur in reasonable amounts in the original mineral a suitable quantity is added. The sulphates are treated with alkali carbonate in an autoclave under pressure. The resulting carbonate mixture is converted to chloride, and some silica is precipitated which carries down a little radium. The silica is worked up separately. From the solution of chlorides the carbonates

are reprecipitated and reconverted to chlorides, which are then submitted to fractional crystallisation.

Up to a certain stage in the fractionation the radium-barium chlorides are used, but the separation is completed with the bromides. The conversion to bromides is usually effected after the concentration of radium has surpassed 20 mg. of radium per kg. of the mixed salts. The methods of fractional crystallisation used and the physical methods recording the progress of the separation are not sufficiently unusual to warrant a full description here.

The Congo pitchblende contains the elements silicon, lead, copper, iron, aluminium, and phosphorus. According to Leemans (quoted by Matignon [1]) (*Revue Scientifique*, 1925, 524–532) the four principal operations are:

(1) Treatment with acids for the elimination and separation of uranium, iron, copper, and phosphoric acid.

(2) Sodium chloride solution is added to eliminate lead, the lead being finally obtained as metal.

(3) Treatment with hydrochloric acid to get rid of calcium.

(4) Treatment with sodium carbonate to eliminate sulphuric acid.

This treatment involves that the radium should first be converted to the insoluble sulphate, the elimination of lead is due to the formation of the lead chloride-sodium chloride double salt, and the elimination of calcium rests upon the easy solubility of calcium sulphate in warm hydrochloric acid. The mixed barium and radium sulphates are converted to the carbonates by means of sodium carbonate. Dissolution of the carbonates in hydrochloric acid then allows of the elimination of silica.

The impurities have now been reduced to $\frac{1}{200}$th part of their original amount, but the mixture of impure radium and barium chlorides even yet only contains one part of radium in 125,000. From this point the work is continued in the manner already described for the working up of carnotite.

During the tedious process of fractional crystallisation

of first the chlorides and then the bromides, lead is periodically removed in small quantities by means of sulphuretted hydrogen. Throughout the crystallisation very pure water is required, since a minute trace of sulphate will precipitate in a form less soluble than the corresponding barium salt.

Radium bromide is usually 95–96 per cent. pure when sold, but an important precaution must be observed. The crystals must be absolutely anhydrous, or else explosive decomposition of the water of crystallisation may occur as a result of the radio-active emission. The crystals must, therefore, be heated to fusion before being finally sealed into glass.

Application of Radium.—Apart from its use in pure science, the only applications of radium are those depending on its luminosity in the dark and its use in medicine. During the war small amounts of radium preparations were used for gun-sights, watches, etc., but the outlet for radium in this direction appears to be very small at the present day.

The therapeutic action of radium may be utilised in various ways. Radio-active matter may be introduced into the blood stream in a state of high dilution, or advantage may be taken of the enormous local intensity of the radio-active effect. This effect is, of course, very complicated, and the analysis of the biological effects of α-particles, β-particles, and γ-rays respectively has not yet been completed. It is probably true to say that the X-rays overshadow the α- and β-particles in importance. The γ-rays are, of course, similar to X-rays, and both exhibit the property of destroying living tissue. The rays are more penetrating than X-rays, and have the advantage of emanating from a very minute source. An overdose of α-rays causes total destruction of the living cells, but in properly regulated doses the rays exhibit a selective effect, leaving some cells intact. The selective effect is due to the fact that those cells which tend to multiply rapidly are most readily attacked. In cancer the area affected is characterised by rapid growth, and the fundamental point

in the radium treatment of cancer is the selective destruction of the cancerous tissue. The degree of selectivity varies enormously, and the danger of the treatment is due to the narrow margin which is frequently observed between the dosages which will destroy healthy and diseased tissues. In many cases of inoperable cancer the skilful use of radium has effected either permanent cure or considerable improvement.

SECTION VII.—BIOCHEMISTRY AND LIGHT

THE subject-matter of this section divides itself quite readily under three headings:

(1) General Effects.
(2) Photo-sterilisation.
(3) Light therapy and Vitamin-D.

GENERAL—THE EYE

The eyes may be harmed by glare, heat, or ultra-violet rays. Against glare and heat there is some protection in the discomfort experienced with excessive radiation; but as nature has not provided a means of recognising ultra-violet rays, it is possible for serious damage to be done without the sufferer becoming aware of the danger. The most harmful rays are on the short-wave side of $340\mu\mu$, and fortunately, a moderate thickness of almost any ordinary glass will not transmit appreciably beyond this point. Excessive exposure of the eyes to ultra-violet rays is followed in a few hours by severe pains (described as "like sand in the eyes"), which can only be relieved in acute cases by the injection of morphine. The condition is known as conjunctivitis, and consists of an inflammation of the conjunctiva, the mucous membrane covering the inside of the eyelids, and part of the eyeball.

A startling instance of the danger of not wearing goggles is given by Kindall.[1] After a demonstration of electric welding which had been witnessed by thirty men, it was found that two, who had been wearing goggles fitted with

thick orange-coloured lenses, suffered no ill-effects. Seventeen men experienced such acute pain that medical treatment for traumatic conjunctivitis was necessary. Those who wore glasses fitted with thin, light-coloured yellow lenses experienced ill-effects varying in intensity.

Any symptoms of conjunctivitis caused by ultra-violet rays should promptly be treated by a doctor.

The eye as an organ does not respond to ultra-violet radiation, and an interesting experiment by Chardonnet [2] shows that the lens filters off the short-wave light. An arc was viewed through a lightly silvered quartz plate transmitting the region 300–343$\mu\mu$ only. It was noticed that persons possessing ordinary vision failed to detect the flickering of the arc through the plate, whilst those from whose eyes the lens had been removed for cataract succeeded in doing so.

Martin [3] examined the absorption spectra of the different eye media and found that the cornea is transparent to all rays longer than 295$\mu\mu$, whilst in the lens absorption commences at 400$\mu\mu$ and is complete at 350$\mu\mu$. Light below 300$\mu\mu$ may thus induce chemical changes in the cornea, and light below 408$\mu\mu$ in the lens. The vitreous humour exhibits a broad absorption band extending from 280$\mu\mu$ to 250$\mu\mu$, with a maximum near 270$\mu\mu$. The significance of this band does not appear to be known.

The vitreous and aqueous humours transmit down to 300$\mu\mu$, but the lens fluoresces strongly with rays between 350$\mu\mu$ and 400$\mu\mu$. This means that in any case extraordinarily little *ultra-violet* radiation can strike the retina. The inflammation which results from exposure of the eyes to ultra-violet radiation is largely confined to the outer structure, and in skilled hands the irradiation of the eye has sometimes proved beneficial.

What of the process of vision itself? This is not the place to follow the question very far, but a brief discussion of one or two aspects of the question may be given. Since 1851 a substance called rhodopsin or visual purple has been known. First isolated from frogs' eyes, it has been

shown to occur in human eyes, and also in those of monkeys, cattle, and pigeons. On exposure to light the purple material undergoes a bleaching process, and according to Eldridge-Green, the mechanism of vision is somewhat as follows :

$$\text{Visual purple} + \text{Light} \rightarrow \underset{\text{(Colourless)}}{\text{Decomposition products}}$$

The products act in some way on the fibres of the optic nerve, and impulses are sent out to the brain ; the rhodopsin is then regenerated in the retina so that a fresh supply is always available. It has been shown by experiments on dark adaptation that the regeneration of rhodopsin is a bimolecular reaction. For the process of vision at low intensities of light it is highly probable that the bleaching is the first action.

A series of fascinating studies has been made by S. Hecht [5] on the photo-sensory process in the clam (*Mya Arenaria*). The clam is a little sea animal possessing a long "siphon," which is retracted by a reflex action on exposure to light. The tip of the siphon moves about 0·5–1·5 cm. towards the shell, but there is always a delay of about two seconds between stimulus and response. This interval—the reaction-time—can be measured accurately. Hecht found that the reaction-time varied with both the intensity and the wave-length of the stimulus. The clam responds most readily to rays about $500\mu\mu$, and much less readily to rays on either side of this value, whilst the response is very nearly zero at $420\mu\mu$ and $620\mu\mu$.

Another very interesting photochemical phenomenon occurs in the response of *Volvox globator* to light of different wave-lengths. *Volvox globator* is found as aggregates of a few thousand cells of a simple river-organism, which tend to move towards any source of light. Laurens and Hooker have shown that the relative stimulating values of lights of differing wave-lengths, indicate quite definitely that the maximum effect is at about $500\mu\mu$, falling again to zero at $420\mu\mu$ and $620\mu\mu$.

We seem in these photochemical reactions to have something unusually efficient, and apparently less complicated than many biological responses.

Vision and these photo-sensory changes seem to be very closely related, and photochemistry has much to discover before it can imitate the processes successfully.

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Animal Luminescence.—Complementary to the photo-sensory phenomena we have just been discussing is the subject of animal luminescence. It may be necessary to justify the inclusion of "animal light" in a book with a bias towards practical applications. In the tungsten filament lamp giving one candle-power for every one and a quarter watts only 3½ per cent. of the energy used is returned in the form of light. In a nitrogen vacuum tube the light energy represents about 8 per cent. of the energy consumed, whilst 90 per cent. of the radiation emitted is in the form of light. The difference between the tungsten lamp and the discharge tube is that in the one case the electrical energy is converted into heat and then into light, whereas in the second case the electrical energy is converted *directly* into light. The latter phenomenon is an example of luminescence. It is clear that, brilliant as are the achievements of electrical science in the development of artificial lighting, the very moderate efficiencies of about 3–4 per cent. present a strong challenge to research. As a problem of finance, the development of "cold light" is a most urgent need.

Dead meat or fish is often observed to be glowing in the dark, a phenomenon due to bacteria living on the food.

Similarly the " phosphorescence " of decaying wood is due to a fungus, and the phosphorescence of the sea is due to numerous varieties of tiny luminous creatures. The *animal* luminescence of the sea differs from the *plant* luminescence of bacteria and fungi, in that it must be stimulated by agitation or other mechanical means.

The fire-fly has likewise to be stimulated into giving off light. There are one or two apparent exceptions in certain luminous fishes. The glow from dead fish is due to bacteria, but one fish found in the East Indies—*Photoblepharon*—possesses a luminous organ about one-fifth the length of the fish itself. As the fish swims through the water it flashes the light on and off by means of a fold of black skin which can be drawn over the luminous organ. Newton Harvey, the authority on animal luminescence, has proved that the light of the luminous fishes *Photoblepharon* and *Anomalops* is due to luminous symbiotic bacteria. Previously the organ had been regarded as a gland, producing a luminous secretion, but this view has now been shown to be untenable. The light organ is very sensitive to lack of oxygen, since, as with all luminous bacteria, light evolution ceases in the absence of oxygen.

Harvey (*J. Franklin Inst.*, 1923, July) says that " other fish and certain kinds of shrimp and squid possess a row of luminous organs along the sides of the body which look like the port holes of a ship at night. . . ."

The luminous organ often possesses a complicated lantern-like structure for directing a beam of light, and contains: (1) A lens-shaped layer of transparent tissue. (2) A layer of photogenic cells. (3) A layer of dark reflecting cells. (4) A black screen almost surrounding it.

The light-producing animals include beetles, centipedes, crustaceans, flies and many other groups, and some of the most valuable and fruitful work has been carried out on the crustacean *Cypridina*.

The chemistry of animal light carries us back to Robert Boyle, who showed in 1667 that the luminescence of decaying wood disappeared as the surrounding air was removed by

means of a pump, but that it reappeared as soon as air was again allowed to enter the apparatus. Subsequent experience has confirmed that oxygen is essential for bioluminescence.

Spallanzani in 1794 dried the luminous tissue from a jelly-fish and found that the light ceased. The tissue could nevertheless be kept unchanged for some time, but as soon as moisture was added the light reappeared. These results have since been extended to other luminescent organisms.

In 1865, Dubois, studying the mollusc *Pholas*, came to the conclusion that the process of light emission was due to the oxidation of material which he called *luciferin*, in the presence of an enzyme *luciferase*. These substances are quite easily prepared. Luciferin is made by adding hot water to the luminous organ of the animal or by quickly heating the luminescent extract of the luminous animal to temperatures which permanently quench the light. The enzyme luciferase is destroyed and the oxidation process is stopped. Luciferase is prepared by allowing a cold water extract of the luminous gland to stand until the luciferin has been completely oxidized. The oxidation can be hastened by aeration, or by adding chloroform, saponin, or sodium glycocholate. The method of preparation means that the enzyme will only be obtained if it is present in excess (in relation to luciferin) in the luminous organ.

When luciferin and luciferase solutions are mixed, light is emitted, but the glow continues only until all the luciferin has been oxidised. Harvey showed that the reduction of the oxidation product can be accomplished in various ways, so that we have :

$$\text{Luciferin} \underset{\text{Hydrogen}}{\overset{\text{Oxygen}}{\rightleftarrows}} \text{Oxyluciferin}$$

or

$$LH_2 + O \rightarrow L + H_2O$$
$$L + H_2 \rightarrow LH_2$$

Luciferin is regarded as closely resembling the proteoses and peptones, whereas luciferase so closely resembles albumin that separation cannot be effected.

Luciferin may be regenerated from oxyluciferin by means of hydrogen sulphide, nascent hydrogen, palladium, and sodium hypophosphate, and by reducing enzymes.

In order to place beyond all doubt the reality of the reduction process, Harvey set up the following elegant experiment. Using platinum electrodes, a current was sent through an extract of *Cypridina* containing luciferase and oxyluciferin and a little salt to make the solution a good conductor. The cathode became covered with a beautiful luminescence, whereas the anode exhibited none. With N/1 sodium chloride the luminescence began to appear at 1·8 volts and was quite marked at 2 volts. This is consistent with the view that the nascent hydrogen reduces oxyluciferin to luciferin, which at once oxidises in presence of luciferase with concomitant emission of light. It is interesting to note that molecular hydrogen will give no luminescence whatever, but freshly cut surfaces of magnesium, aluminium, manganese, zinc, and cadmium luminesce when placed in the oxyluciferin-luciferase-oxygen solution. Of these metals only magnesium will liberate hydrogen in bubbles from water, but in all of the above cases a film of atomic hydrogen must be formed.

In the salt-oxyluciferin-luciferase-oxygen solution platinum does not glow, but if it is touched with zinc, cadmium, or aluminium, a bright luminescence at once appears at the surface of the platinum.

The explanation is clear in terms of the circuit which is set up by metallic contact. It is significant that in the presence of palladinised gauze and colloidal platinum or palladium it is possible to maintain a continuous luminescence by passing hydrogen from a cylinder into the oxyluciferin-luciferase solution.

Harvey points out that here there is a means for producing a luminescent lamp which would burn indefinitely (unless secondary reactions interfere), provided a slow stream of hydrogen and oxygen be supplied. Whilst admitting that the light is too weak for purposes of illumination, and agreeing that the reaction is a mere scientific curiosity at

the present time, Harvey rightly insists that the principle is a very important one. There is no *à priori* reason against finding theoretically similar reactions in which the light-emission is on a larger scale.

The instances of intensely bright chemiluminescence with which we are acquainted, *e.g.* Kautsky's siloxen-adsorption compounds (*Trans. Faraday Soc.*, October, 1925, "Photochemical Discussion") do not show reversibility in the same way.

The physical study of animal light shows that all the light is in the visible part of the spectrum, a most important fact, since it shows clearly that the production of "cold" light can be accomplished. In order to give some idea of the intensity of animal light, Harvey states that the measurements carried out by Ives on the candle-power per unit area in the case of the glow-worm indicate that a disc of light of that intensity (0·0144 lumen per sq. cm.) would need to be 2 metres in diameter to give a comfortable light for reading in a room with a ceiling 3 metres high and a table 1 metre high.

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Harvey and R. F. Morrison, "The Minimum Concentration of Oxygen for Luminescence by Luminous Bacteria" (*J. General Physiology*, 1923, **6**, 13–19).

Harvey, "Production of Light by the Fishes *Photoblepharon* and *Anomalops*" (Carnegie Inst. Washington, Publication No. 312).

Action of Light on Proteins, Enzymes, Blood, etc.—Bovie studied the action of ultra-violet light on certain constituents of protoplasm with a view to explaining the actions with living cells. Fresh egg-albumen was completely coagulated at room temperature by quartz-mercury radiation (35 hours: 10 cm. from lamp to material). An aqueous solution of egg-albumen was coagulated rather more quickly, the coagulum settling down at the bottom of the test-tube.

Crystallised egg-albumen, freed from ammonium sulphate by dialysis, could be coagulated in glass tubes, showing that with the pure material, the very short wave-lengths were not essential. The coagulum does not appear to be chemically different from albumin coagulated by heat in the ordinary way. Experiments by Bovie and his colleagues,[2, 3, 4] on the action of light on the organism *Paramecium caudatum*, show that sublethal exposure to ultra-violet rays renders the organism extremely sensitive to heat, so that it is injured or killed by amounts of heat which it could have borne with safety before exposure to light. It is as though the initial effect of the light is to cause a small change which is capable of being greatly magnified by metabolic changes occurring at higher temperatures. Burge[5] was able by means of ultra-violet irradiation to produce cataract in fish living in dilute solutions of calcium salts or sodium silicate. His view is that the protoplasm undergoes photo-chemical change, endowing it with enhanced reactivity, and that the salts which then combine with it, effect coagulation. Clark[6] observed that irradiation of solutions of egg-albumen causes the formation of larger aggregates only if the albumen particles are negatively charged, whereas when they are positively charged (or even uncharged) the ultra-violet light reverses the coagulation process—actually increasing the dispersity. In order to harmonise these results with current colloid chemistry it is necessary to assume that the light liberates electrons at the albumen surface and that the primary change is photo-electric.

Pincussen[7] has studied the destruction of diastase by means of ultra-violet rays. He finds that sunlight has no effect, but that with quartz-mercury radiation, a solution at p_H 4·6 loses its activity with extraordinary rapidity.

A great variety of conclusions are available as to the effect of irradiation on the blood; the subject is an intricate one, and a few effects will merely be mentioned for the sake of illustration.

It seems fairly clear that the exposure of the human body to sunlight causes an increase in the blood-alkalinity,

and that this change usually occurs concomitantly with pigmentation of the skin. Hæmoglobin, blood sugar, viscosity, and coagulation do not appear to be influenced much by irradiation. One effect of the light is apparently elucidated in the formation of vitamin-D in the skin (see p. 217), but how far subsequent changes follow from this we do not know. It is thought by many that light increases the bactericidal power of the blood, but it must not be forgotten that the *primary* photochemical process or processes in the irradiation of the body must occur in the first few hundredths of a millimetre of skin. The blood can only be affected somewhat indirectly, and in reading the literature this point should not be forgotten. The chemistry of the subject is still very obscure, even if the medical aspects are as well understood as might be concluded from the literature of actinotherapy.

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PHOTO-STERILISATION

In 1877, Downes and Blunt [1] found that the ordinary organisms present in decaying matter were readily killed by ultra-violet rays, and that it was just as easy to kill the bacteria in dry as in moist materials. For some time it was generally believed that free oxygen was essential to the bactericidal action, but in 1892 Ward [2] established definitely that this view was mistaken. He observed that although the violet rays of the solar spectrum exerted some little effect, almost the whole of the bactericidal action was due to ultra-violet rays. The carbon arc gave a very marked effect, which was only slightly diminished by the interposition of a quartz plate, but which fell almost to zero when a glass

plate was placed between the light and the culture. Clearly the effective wave-lengths must lie on the short-wave side of 340$\mu\mu$, since this is about the wave-length at which glass ceases to transmit freely. This result makes it clear why the misconception arose as to the necessity for oxygen in the bactericidal process. In order to exclude oxygen, glass vessels were used and the active rays were thereby excluded as well!

Although a good deal of work was carried out in various directions, notably by Bie and Bang on the effect of visible light of different colours, it was not until 1903 that a definite step forward was taken.

Bernard and Morgan [3] projected the spectrum of a carbon arc on to an agar plate superficially inoculated with *Bacillus coli communis*. After a definite time had elapsed the plate was incubated, and by noting the positions and wave-lengths at which the bacteria had survived the irradiation process, it was possible to arrive at definite and important conclusions.

In the first place, it was found that the bactericidal rays lay between 329 and 226$\mu\mu$, and that on either side of these limits the bacteria were not killed. In the second place, it was stated that the bactericidal rays possessed so little power of penetrating the body tissue that there was no hope of using the sterilising action *in vivo*. Thirdly, it was concluded that the known therapeutic effects of light were due to rays longer than 330$\mu\mu$.

In 1917 Browning and Russ [4] carried out similar experiments, using a gelatin plate inoculated with *Staphylococcus pyogenes aureus*, and as a light source the tungsten arc. A very sharp line of demarcation was observed at 296$\mu\mu$, longer waves not affecting the bacteria, whilst shorter waves were markedly lethal, especially between 254 and 280$\mu\mu$.

Browning and Russ go on to say that "from the clinical point of view" there are two distinct regions of ultra-violet radiation:

Group 1.—A portion which begins where vision fails, namely, 3,800 and extends to 2,960 Å.U. These rays have no marked germicidal, action, they are capable,

however, of penetrating a considerable thickness of human skin.

Group 2.—A portion which extends from 2,960 to nearly 2,100 Å.U. These rays have very marked germicidal action, the region of maximum effectiveness being between 2,800 and 2,540 Å.U. The penetrating power of these rays is, however, very small; they are completely absorbed by as little as 1/10 mm. of human skin.

These authors also photographed the tungsten spectrum through an emulsion of bacteria, and found that all rays on the short-wave side of 297$\mu\mu$ were absorbed. Henri [5] reported a parallelism between the absorption curve for protoplasm and the spectral distribution of bactericidal activity. It is known that among the constituents of the protein molecule are numbered the aromatic amino acids tyrosine and phenylalanine. These substances exhibit selective absorption between 248 and 271$\mu\mu$, and can be used as filters for screening off that region of the spectrum. Used in this way, they protect the bacteria from the destructive action. There is therefore good reason to suppose that the mechanism of photo-sterilisation consists *in the first instance* in a change suffered by aromatic amino acids in the protein. At any rate, it has proved quite impossible to maintain the view that germicidal substances such as hydrogen peroxide or ozone are responsible for the effects observed.

Considerable variations are observed in the photosensitivity of bacteria of various species. Von Recklinghausen (cited by Ellis and Wells, *Chemical Action of Ultra-Violet Rays*, p. 247) found that under standard conditions, *B. cholera, B. typhoid, B. dysentry, B. coli* were very readily destroyed, and *B. anthrax* (*sporogenus*), *pneumobacillus* and *sarcina alba* only a little less readily. The following were about twice as resistant as the first group of organisms: *B. tetanus, B. megatherium, B. phleole, B. subtilis, sarcina lutea. Paramecia* and *yeast* require respectively about 10 and 20 times as long as *B. coli*.

The differences in resistance have been turned to practical account in various ways; for instance, vaccinia virus may be "sterilised" by ultra-violet light, since the harmful bacteria are much more sensitive to the irradiation process than the more desirable organisms. In the same way the partial photo-sterilisation of milk allows the desirable lactic acid bacteria to survive whilst disposing of many disease-bearing organisms.

The low penetrating power of ultra-violet rays into living tissue has already been referred to, but it is necessary to give quantitative data, if the true position is to be realised. The data of Glitscher and Hasselbach [7] given below are in excellent agreement with observations carried out by Dr. E. D. Kamm and the author.

TRANSMISSION OF EPIDERMIS

Wave-length in $\mu\mu$.		Percentage transmission 0·1 mm. Thickness.	Percentage transmission 1 mm. Thickness.
Rays harmless to most bacteria ..	436	59	0·5
	405	55	0·3
	366	49	0·08
	354	42	0·02
	313	30	—
	302·5	8	—
"Abiotic" or bactericidal rays	297	2	—
	289	0·01	—

It will be seen that Bernard and Morgan had ample reason for stating that sterilisation *in vivo* was impracticable. Subsequent experience has, however, shown that the bactericidal action of light has a distinct claim to utility in certain types of open wounds; although it is inadvisable to dogmatise as to the exact way the beneficial effect is exerted.

Let us consider the industrial use of photo-sterilisation. For purifying water the method has several advantages:

(1) The cost is not great.
(2) There are no undesirable secondary reactions, nor is the water affected by the light.
(3) Sterilisation may be carried to completion without the use of chemicals—a consideration of some importance to surgery and to certain food preparations.

On the other hand, the water must be clear if the process is to be effective. Turbid water needs to be clarified in some way, since the presence of opaque particles considerably reduces the effective range of a light source, and, furthermore, deposits may form on the quartz. The second objection is that the deterioration of quartz lamps occurs first in the region of bactericidal rays, so that photosterilisation needs to be accurately controlled.

An analysis of the patent literature shows that investigators have aimed at:

(*a*) Increasing the proportion of short-wave ultra-violet radiation in the output of the light source.

(*b*) Devising means for rapidly circulating very thin films of liquid in front of the light.

(*c*) Providing spraying arrangements for utilising as large a solid angle as possible about the source of light.

The water-cooled mercury vapour lamp is generally admitted to give the highest intensity of suitable radiation, since the cooling hinders the formation of an absorbing non-luminous layer of mercury vapour in the arc-tube, and so increases the output of ultra-violet rays. The liquid to be sterilised may be pumped rapidly between long concentric tubes, so that the lamp will then operate similarly to a water-cooled lamp. In several processes systems of rotating drums have been used to pick up a thin film of liquid, which is then exposed to the light for a brief period. This method can readily be adapted to the simultaneous drying and sterilising of milk, or, in fact, to the irradiation of any solution from which the solvent is to be removed. In such cases it must be remembered that the solvent vapour will occur in the light path, and only solvents of very low absorptive power for rays in the middle ultra-violet are permissible, *e.g.* water, alcohol, but *not* acetone, benzene, etc.

Many processes have been suggested for sterilising milk by means of ultra-violet light, but considerable difficulties have been encountered, because the milk is liable to develop

an unpleasant taste, and the oxidases present may be destroyed. On account of the low transmission of an emulsion such as milk it is difficult to secure complete sterilisation without undesirable effects on the nutritive properties. Helbronner and von Recklinghausen state that the most efficacious method consists in a preliminary heating above 60° followed by ultra-violet irradiation. It is customary in certain margarine factories to sterilise whole milk as soon as it enters the works by employing a method involving heat and ultra-violet. The cream is then separated centrifugally and used separately, whilst the skim-milk is used as a medium for the growth of pure cultures, and is later mixed with the margarine to give the product a butter-like flavour. As will be seen later, it is probable that irradiation of the milk has resulted in the photosynthetic formation of vitamin-D. Feeding tests have shown that the amount of growth promoting vitamin-A present in milk is reduced by irradiation, whilst the amount of anti-rachitic vitamin-D is greatly increased. It is perfectly feasible for vitamin-D prepared by a photochemical process to be added to margarine.

The outstanding problem concerning the irradiation of milk is the discovery of the wave-lengths which destroy vitamin-A. If these waves are between 300 and 370$\mu\mu$, as there is some reason to believe, it should be possible by means of light screens to protect the vitamin-A from destruction, while allowing the bactericidal reaction and the formation of vitamin-D to go on with unimpaired efficiency.*

In an interesting patent, Henri, Helbronner and Recklinghausen claimed that "the taste and colour of young wine are changed by ultra-violet light, so that in a few minutes the liquor assumes the characteristics of old wine." Ellis and Wells (*loc. cit.*) state that before the war this method of ageing wine was making substantial headway in France.

* Cod liver oil, containing A, D and ergosterol might well be irradiated with such a screen.

In the *Engineering News Record* (1917, 1021) Smith describes an installation for the sterilisation of water by ultra-violet radiation at Henderson, Kentucky. Up to 3,500,000 gallons of filtered water were sterilised daily for some months at a current consumption of 92·5 kilowatt hours per million gallons.

It must nevertheless be admitted that relatively few installations are now in operation and that large scale application has been slow.

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LIGHT THERAPY

The treatment of disease by radiation has been practised since very early times. Under the names heliotherapy, radium-therapy, X-ray therapy, and ultra-violet or actino-therapy, the subject has by now an enormous literature. Recent years have witnessed great expansion in actino-therapy, and to-day the provision of lamps and accessories has become quite an industry. It is believed that the rays which are absorbed by the skin exert some special effect either of a chemical or physical nature; in other words, that the beneficial results are not due merely to a heating effect. The Turkish or heat bath, and the ultra-violet light bath are both valuable methods of treatment, but they are radically different in their mode of operation.

Modern light therapy began with the work of Finsen in 1893. The principal success of this worker was with lupus, a tubercular skin disease very difficult to cure. Over 1,100 out of about 1,200 cases were greatly improved as a result of the treatment, which had, however, the disadvantage of being tedious and costly. A second phase in light therapy began in 1903 with the establishment of Rollier's sanatoria at Leysin, in Switzerland, for the treatment of tuberculosis by means of sunshine. Very striking results have been obtained, especially with surgical tuberculosis, and the sun cure has become a part of medical practice and a fashion amongst holiday makers.

It was suspected that the success of the Finsen and Rollier treatments was really due to ultra-violet light, and with the advent of the quartz-mercury vapour lamp the suspicion has now become a certainty. It is well known that only a selection of the wave-lengths emitted by the sun actually reach the earth, because of absorption by the atmosphere. This absorption is greater in moist dust-laden air than at high altitudes, where the air is dry and clean. On a clear day the amount of radiation at 6,000 feet is roughly one and a half times that reaching the earth at sea-level. Ultra-violet rays are very readily absorbed

by slightly impure air, and a smoky atmosphere further increases the screening effect. Given clean air, it is not necessary, however, to expose a patient to *direct sunlight*, as there is always a considerable indirect ultra-violet radiation from blue sky. Heliotherapy has been more successful in the high Alps than elsewhere, not only because of the large amount of ultra-violet radiation available, but also because the snow absorbs heat rays and reflects ultra-violet rays.

In order to illustrate the views held at the present time by representative medical men, the following quotation may be given from an "Interim Report on Artificial Light and X-ray Therapy," by L. D. Cruickshank and E. Watt (published by the Scottish Board of Health, 1925, 1s.):

"Nature appears to have determined a limit to the functional activities necessary for perfect bodily health. In other words, the aim of nature is to secure a perfect adaptation of man to his proper environment. An average limit of growth in relation to age, and a functional activity of the bodily organs adequate for the needs of the various stages of growth, are the fundamental facts on which physiological knowledge is based. But we know of no means by which we can add 'one cubit to our stature' or by which we can, with benefit, stimulate function beyond 'normal' limits. Hitherto where growth has been deficient or function defective we have had recourse to material remedies. In ultra-violet radiation a new form of treatment is at command. The extent of its therapeutic uses is as yet unknown, but experimental investigation has shown that its therapeutic properties are in the main limited to conditions of growth or of function that are below normal. For example, it has been found to increase body weight, to increase the rate of growth, to improve the mineral content of the blood, to increase the functional activity of the endocrine glands, to increase the bactericidal power of the blood, etc., where these are below normal, but to have no corresponding effect on normal individuals. We found in the course of our inquiry that without excep-

tion every patient undergoing ‘ light treatment ’ experienced an improvement in his or her general feeling of well being, apart altogether from improvement or otherwise in the disease for which the treatment was being given.”

The action of visible radiation is described as “ leading to a dilatation of the cutaneous vessels, stimulating the sweat glands and aiding in the relief of deep-seated congestion.”

In weighing the advantages and disadvantages of different light sources, these authors observe that a quartz-mercury vapour lamp is much more economical to run than the carbon arc. Writing of the vacuum type of lamp, they state “ the effective life of the lamp is said to vary from 1,000 to 3,000 hours. Owing to its construction it cannot be cleaned, and when its irradiating power is seriously diminished it must be renewed at considerable cost.” The atmospheric burner (*e.g.* K.B.B. type) can be transported empty and filled with mercury by the user. After running for some time it may easily be reconditioned. The water-cooled mercury lamp is recommended for local treatment, but it is described as “ less serviceable in public clinics where general irradiation is the common practice.” The large metal cases which are frequently supplied with mercury lamps can be dispensed with in clinics.

Carbon arcs using 10, 25, 50, and 75 amperes are all in use in various places, but the arc most commonly preferred is the 25–30 ampere lamp. Carbon electrodes impregnated or cored with metals or oxides are often used, but there is at present little trustworthy information concerning the degree to which the specially prepared carbons are superior to ordinary carbons for the special purposes of actinotherapy. Hill recommends a “ long flame ” arc as giving a richer ultra-violet output than the ordinary arc, but this type of lamp flickers very readily. Open carbon arcs are expensive, owing to the necessity of using resistances to cut down the voltage to 50–70 volts.

Tungsten arcs have in their favour a very rich ultra-violet spectrum packed with lines of fairly even intensity.

The running cost is less than that of carbon arcs, but the electrodes are more costly, although prices have lately shown a downward tendency. The principal objection to metallic arcs is that they give off fumes which may be harmful.

Diligent inquiry has convinced the author that it is very difficult to say which is the best light source for actinotherapy. As Cruickshank and Watt say, "experts seem to favour the lamp they have used most."

In administering ultra-violet light the usual method is general irradiation, beginning with brief exposures of a part of the body and gradually increasing both the time and the area exposed, but the regulation of dosage presents a very difficult problem. Exposure to sunlight or ultra-violet rays produces a redness of the skin known as *erythema*, which is followed, if exposure is sufficiently prolonged, by tanning or sunburn. Pigmentation is regarded as Nature's attempt to provide protection against too much ultra-violet light. Perhaps it is true that at the present time the best guide to dosage is the degree of erythema which results after a test exposure, since most other methods take no account of the idiosyncrasy of the patient.

The experience which has so far been gained goes to show that non-pulmonary tuberculosis, rickets, malnutrition, and certain skin diseases respond well to treatment. Lupus is very frequently cured, and in some cases considerable improvement has been noticed in arthritis. Two definite mechanisms which have a chemical bearing have been suggested for curative processes.

(*a*) The photosynthesis of vitamin-D (to be discussed later).

(*b*) An increase in the bactericidal power of the blood.

For both changes there is a possibility of over-dosage. It is not known whether the reactions run parallel, neither is it known whether the activating wave-lengths are the same in the two cases.

As a working hypothesis it may be assumed that ultra-violet irradiation helps to regulate calcium-phosphorus

metabolism by means of the formation of vitamin-D, and at the same time increases the resistance of the blood to noxious bacteria.

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Vitamins and Light.—At present there are supposed to be five vitamins, designated A, B, C, D, E, each of which has been detected as the result of skilfully conceived feeding experiments. Of the five vitamins, B and C do not concern us here. E is a new-comer, and beyond its function in influencing fertility together with a suspicion that it is chemically related to the sterols we know little about it. Both vitamins A and D are fat soluble. A acts as a growth promoting catalyst, and in its absence a special eye disease called xerophthalmia appears, whilst D is known as the anti-rachitic vitamin, because of its curative action in rickets and other diseases concerned with faulty calcium metabolism.

The existence of the *two* vitamins A and D was not at first realised, and the properties which we now associate with D were ascribed to A. For simplicity we shall refer to a diet deficient in growth-promoting, anti-xerophthalmic and anti-rachitic factors as showing A′ deficiency. Rats fed on such a diet showed all the expected symptoms, which, however, disappeared if a small daily dose of cod-liver oil was administered. The next step was the discovery

that, provided they had access to the light, rats fed on a diet deficient in A′ did not develop rickets.[2] Neither, on the other hand, did rats kept in the dark and given an adequate diet. At the same time it was reported by Huldschinsky[3] that infantile rickets could be cured by exposing the body for brief periods to the light from a quartz-mercury lamp. It appeared plausible to connect the high incidence of rickets in the winter months with a deficiency in sunshine, and the work of Hess and Unger[4] established the possibility of curing the disease by sunlight.

It rapidly became clear from the work of a group of American investigators[5] and of Miss Hume[6] in England that ultra-violet light could replace cod-liver oil, as far as the prevention of rickets was concerned, but that it could not fulfil all the anti-xerophthalmic and growth-promoting functions of the oil. In the terms used to-day light cannot synthesise vitamin-A in the body, but it can act as a substitute for vitamin-D.

At this stage the differentiation between vitamin-A and vitamin-D had become apparent, and obviously their effects would have to be clearly separated. Pappenheimer and Weinstock[7] took a step forward when they concluded that the effective rays in the cure of rickets were on the short-wave side of $313\mu\mu$.

The next significant step in the history of vitamin-D is of extraordinary interest. Hume and Smith[8] found that rats kept in glass jars which were exposed to a quartz lamp for 10 seconds on alternate days maintained normal growth longer than control rats fed on a diet deficient in the same factors. The implication that the air in the jar could be activated by the rays was negatived by Webster and Hill,[9] who only managed to secure the curative effect by shining the light on the animals themselves. Hume and Smith[10] retorted that rats on a rickets-producing diet and housed in previously irradiated glass jars containing sawdust were as healthy as those undergoing direct irradiation. *In the absence of sawdust the rats showed the usual symptoms of rickets.*

About the same time Steenbock, working with Black and Nelson,[11] had discovered that various foods, and in particular fats which in the ordinary way conferred no protection against rickets, became anti-rachitic on exposure to ultra-violet rays. It was claimed that the illumination of food caused it to become growth promoting and anti-rachitic, and a patent was taken out to that effect.[12] A considerable variety of substances show this effect, *e.g.* cotton-seed and linseed oils become anti-rachitic if exposed to thin layers for two minutes at a distance of one foot from the mercury lamp.

MATERIALS TESTED FOR VITAMIN-D POTENCY AFTER IRRADIATION

Positive.	Negative.
Lettuce (green or yellow).	Mineral oil.
Vegetable oils.	Gelatin.
Sawdust.	Air.
Wheat.	Water.
Cholesterol.	Blood serum.
Phytosterol.	Chlorophyll.
	Hæmoglobin.

The conclusion forced itself on many different researchers that vitamin-D could be produced photochemically from some substance common to many naturally occurring foods.

The next step in the story concerns the investigations of Drummond [13] on the chemical nature of cod-liver oil. It was found that by hydrolysing the oil (which is rich in both A and D) by means of a boiling solution of caustic alkali under conditions preventing oxidative changes, it was possible to extract both vitamins, unchanged as regards physiological activity, by means of light petroleum or ether. Drummond found further that the full vitamin activity was concentrated in the unsaponifiable fraction, which represented about 1 per cent. of the original oil. By crystallisation from methyl alcohol at low temperatures and subsequent precipitation with digitonin, all the cholesterol was removed without affecting the vitamin activity of the residual red-brown oil which corresponded to about 0·4 per cent. of the original cod-liver oil. Attempts to isolate active

fractions from this material were of little use, owing to the presence of considerable amounts of resinous substances formed during saponification. These were to some extent removed by subjecting the material to distillation in superheated steam, in an atmosphere of nitrogen. The purified material appears on analysis to consist very largely of unsaturated alcohols probably allied to the hydro-aromatic or terpene group.

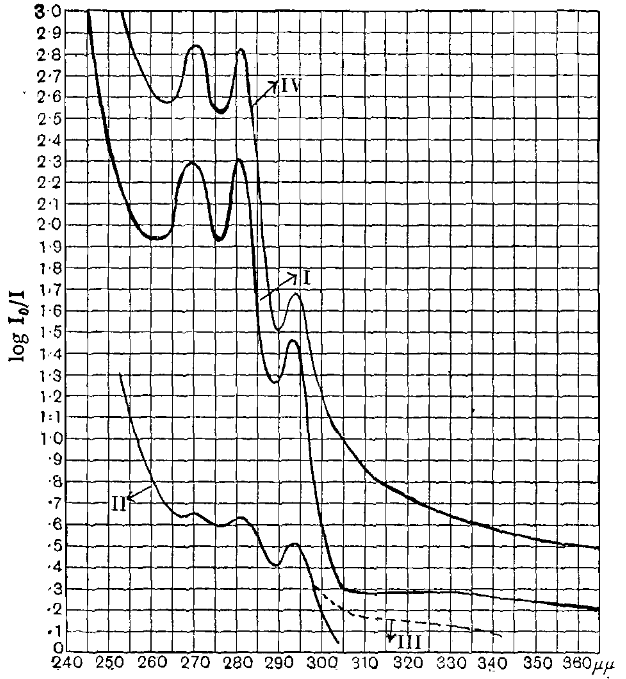
Drummond's brilliant work thus established, that up to a certain point in the separations, the two vitamins followed the cholesterol in the unsaponifiable part of the oil. This indicated that the vitamins resembled cholesterol in chemical nature, but that cholesterol itself was inactive.

A further discovery has thrown still more light on the subject. When cholesterol (obtained from brain and rigorously purified) is subjected to irradiation, this previously inactive material now acquires anti-rachitic properties.

When we remember that skin contains an appreciable amount of cholesterol, it is difficult to resist the conclusion that a part at least of the curative action of ultra-violet light on the body can be traced to the synthesis *in vivo* of vitamin-D. When, however, we look more closely into the matter we find that the association of curative properties with cholesterol is no more than a clue. If cholesterol is subjected to bromination and then to reduction with sodium amalgam, the product would be expected to be identical with the original material. The product actually obtained is identical with cholesterol in every respect but the significant one, that it no longer acquires anti-rachitic potency on irradiation. It would therefore seem as if cholesterol contains a small amount of some closely related material.

Now, since a photochemical change occurs on irradiation of ordinarily purified cholesterol, so that the product becomes endowed with anti-rachitic potency, it follows from the Grotthus-Draper Law (p. 3) that since it is only those wave-lengths which are absorbed which induce photochemical change, the absorption spectrum of cholesterol

should be worthy of study. Hess and Weinstock[14] observed that when cholesterol was irradiated by means of ultra-violet rays, a change in the absorption spectrum occurred. The activated material absorbed light of certain wave-lengths rather less than did ordinary cholesterol, a difference in the absorption over the entire range of wave-lengths



Cambridge University Press.] [*Biochemical Journal.*

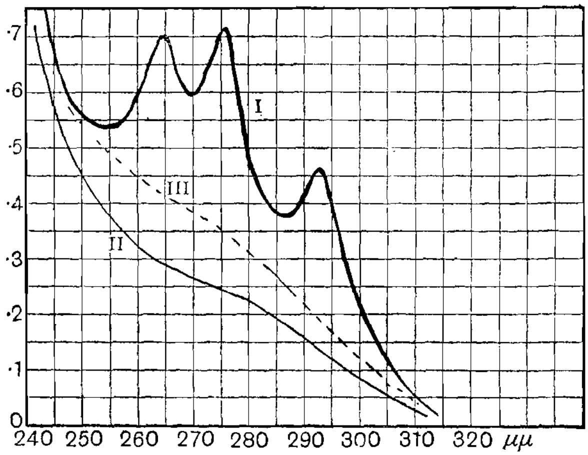
FIG. 25.

I. Cholesterol (least soluble fraction) ether solution.
II. Ordinary *purified* cholesterol, m.p. 148·5°.
III. Solution II. after standing 1 hour.
IV. Cholesterol (least soluble fraction) in alcohol (2 grms. in 50 c.c., 4 cm. cell).

(integrated) being detected by the use of a thermopile and galvanometer set. Schlutz and Ziegler,[15] carrying the matter further, observed that carefully recrystallised cholesterol, melting at 148·5° or very near that point, showed selective absorption of "wave-lengths between 294–296μμ and 279–294μμ with a great deal of general

absorption beyond 294$\mu\mu$." The absorption bands, which were evidently very shallow, could not be detected in alcoholic solution but showed up in ether or chloroform. Moreover, the bands were only observed in the first crop (five fractions collected) from a fractional crystallisation from alcohol of cholesterol (m.p. 148·5°), which had previously been recrystallised seven times from the same solvent.

A quantitative study of the absorption spectrum of cholesterol was made by Heilbron, Kamm, and Morton.[16] The curves for ordinarily purified cholesterol showed



Cambridge University Press.] [*Biochemical Journal.*

FIG. 26.

I. Least soluble fraction from cholesterol.
II. Cholesterol after removal of active compound.
III. Irradiated fraction.

clearly the bands recorded by Schlutz and Zeigler, but the shape of the curve indicated that it was made up of two separate curves, one of which was regarded as due to cholesterol itself and the other to the material which became active on irradiation (Figs. 25 and 26).

In order to test this view, cholesterol was subjected to fractional crystallisation from ethyl acetate. It was definitely established that ordinary cholesterol contained another compound in small quantity, and that this could be accumulated in the least soluble fraction. The intensity

of selective absorption was four times as great in this fraction as in the original cholesterol. A sample of the concentrated product was irradiated and tested biologically by Rosenheim and Webster, and the anti-rachitic activity was found to be three to four times as great as that of a sample of the non-concentrated material.

The impurity present in cholesterol was shown to exhibit three absorption bands with maxima at 293·5, 281·5, and 270$\mu\mu$ respectively. These bands disappeared on irradiation and the substance acquired anti-rachitic potency. This work was soon confirmed by Pohl,[17] who had arrived at the same conclusions independently. It became clear that the appearance of the three absorption bands provided a criterion for the presence of an X-substance and consequently for the occurrence of the reaction

$$\text{X-substance or vitamin precurser} \xrightarrow{\text{light}} \text{vitamin-D}$$

Now, it was known that the precursor was readily destroyed by oxidation, that it was very probably a sterol, but that it did not give a precipitate with digitonin, nor did it show all the typical sterol tests in quite the usual manner. The probability was that either a sterol or sterol derivative would turn out to be the elusive X-substance.

The nature of provitamin-D, as it is now called, was solved by a strong combination of investigators.[18] Rosenheim and Webster had carried out many pioneer investigations on the biochemical side, whilst Windaus had devoted many years to the study of the pure organic chemistry of the sterols, and Pohl had measured the absorptive properties of the X-substance. Working in collaboration, these investigators showed:

(*a*) That ergosterol, a sterol derived both from ergot of rye and from yeast, and in its structural formula possessing three double bonds, showed the three absorption bands with great intensity.

(*b*) That on irradiation by means of a quartz-mercury lamp the bands disappeared and that the resultant product exhibited enormous anti-rachitic potency.

It was therefore concluded that the provitamin was either ergosterol or a very similar sterol.

In extension of their earlier work, Morton, Heilbron and Kamm [19] examined the absorption spectrum of ergosterol before and after irradiation. It was found that the three bands observed in ordinary cholesterol were reproduced with great accuracy when ergosterol was used. The relative intensities of absorption indicated that the concentration of ergosterol in cholesterol was of the order 10^{-3}. The change in the absorption of ergosterol brought about by irradiation of alcoholic solutions was then followed by means of the spectroscope. Samples were withdrawn every 15 minutes from a solution containing 0·05 gram of ergosterol in 250 c.c. of optically pure alcohol.

A description of some of the absorption curves is given below (see Fig. 27):

(1) Ergosterol. Fresh solution not irradiated. Bands at $270\mu\mu$, $281{,}5\mu\mu$, and $293{,}5\mu\mu$, minimum $230\mu\mu$, ϵ max. 10,200, ϵ min. 2,400.

(2) Irradiated for 30 minutes. Broad maximum near $275\mu\mu$, ϵ max. 8,500, minimum near $230\mu\mu$, ϵ min. 3,750. The absorption band is wider in the region 230–$265\mu\mu$ than the corresponding curve for the fresh solution.

(3) Irradiated for 60 minutes. Broad maximum near $275\mu\mu$, ϵ max. 7,000, minimum near $230\mu\mu$, ϵ min. 4,850. The curve shows a marked step-out in the region 240–$260\mu\mu$, indicating the incipient appearance of a band in that region of the spectrum.

(4) Irradiated for 90 minutes. The curve shows a new maximum near $247\mu\mu$, ϵ max. 6,300, and a minimum near $230\mu\mu$, ϵ min. 5,800. The persistence of the new band is thus low. At the same time the absorption curve shows marked absorption over the region 260–$300\mu\mu$, indicating that the ergosterol has not entirely disappeared.

(5) Irradiated for 120 minutes. The band at $247\mu\mu$

has increased in persistence, whilst the absorption over the range 260–300$\mu\mu$ shows a collateral decrease.

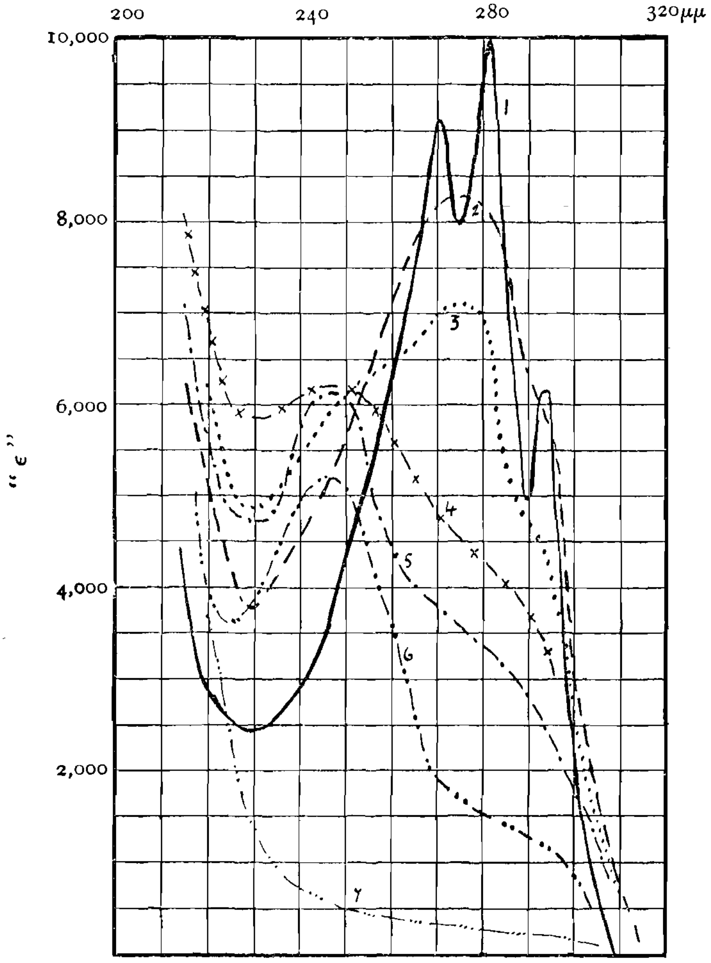


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FIG. 27.
Ergosterol.

1. ———— *Fresh solution.*
2. - - - - *Irradiated for* 30 *mins.*
3. . . . . . . „ „ 60 „
4. —×—×—„ „ 90 „
5. —·— *Irradiated for* 120 *mins.*
6. —··— „ „ 150
7. —···— „ „ 6 *hrs.*

(6) Irradiated 150 minutes. The band at 247$\mu\mu$ is well developed, ϵ max. 5,250, and a minimum is shown

at 225$\mu\mu$, and the persistence is considerable. From 247$\mu\mu$ to 269$\mu\mu$ the absorption curve is fairly straight, but at 270$\mu\mu$ a sharp inflexion commences and the curve falls slowly to the limiting position near 310$\mu\mu$.

(7) Irradiated for 6 hours. The solution is now almost diactinic, and all trace of selective absorption has disappeared.

The curves (Fig. 27) show that the reaction

$$\text{Ergosterol} \xrightarrow{\text{u.v. light}} \text{Vitamin-D}$$

is accompanied by the disappearance of selective absorption in the region 260–300$\mu\mu$, and by the appearance of a new selective absorption in the region 230–260$\mu\mu$ with a maximum of 247$\mu\mu$. This new band itself disappears with further irradiation, a fact which is not inconsistent with the view that it is due to vitamin-D, since it is known that "excessive" irradiation of cod-liver oil induces a loss of vitamin potency.

When the extinctions at 270–275 and 280$\mu\mu$ are plotted against time the result is within experimental error, a straight line indicating that the rate of disappearance of ergosterol depends solely on the energy input. By plotting the persistence of the new band against time, a roughly linear relation is likewise obtained. These results can only mean that the *whole* of the incident energy is absorbed and is photochemically effective, within the absorption band and within the limits of the straight line relationship.

Morton, Heilbron and Kamm conclude that the irradiation of thin layers of solid ergosterol is unsatisfactory. Complete disappearance of the bands is only secured after long periods of exposure and under conditions not precluding consecutive reactions.

The absorption curves indicate a fact of considerable significance, namely, that the irradiation of ergosterol in solution or in the solid state is quite unlikely to give pure vitamin-D, unless special precautions are taken. The existence of a well-marked absorption band between 225$\mu\mu$

and $270\mu\mu$, characteristic of the photochemically unstable vitamin-D, means that if photo-decomposition of this compound is to be avoided, *these radiations must be screened off*. The most suitable material from the point of view of transmitting only the middle ultra-violet region is the proprietary "Vitaglass." Since, however, the rays between $270\mu\mu$ and $293\mu\mu$ are absorbed to no inconsiderable extent

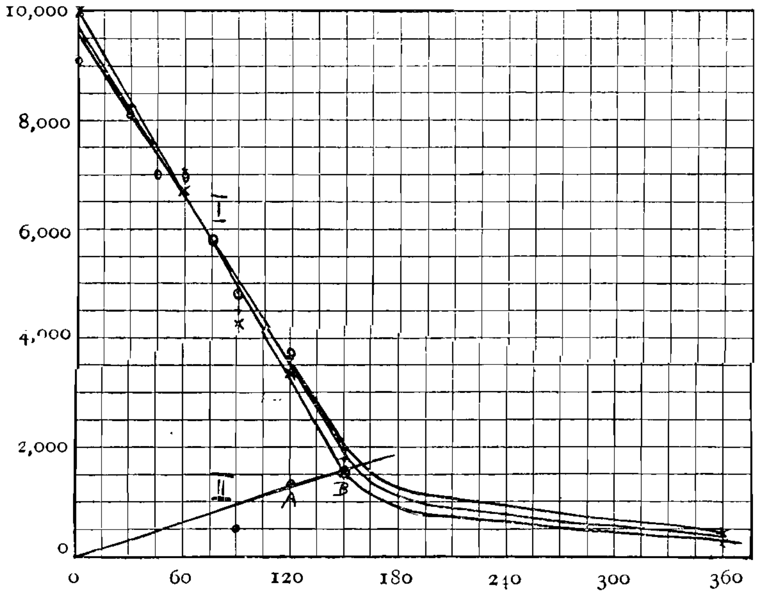

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FIG. 28.

Exposure in minutes.

I. *Extinction of coefficients at* $281{\cdot}5\mu\mu$, $275\mu\mu$, $270\mu\mu$, *ergosterol curves.*
II. *Persistence of new band (line AB produced cuts axes at origin).*

by vitaglass, very prolonged exposures will be necessary. Rosenheim and Webster state that "the action of ultra-violet light on ergosterol leads to an obvious physical change and the production of a yellowish resin. The nature of the intramolecular change which gives rise to the vitamin formation is at present unknown. The first step towards solving this problem is the preparation of pure vitamin-D, and at present the line of attack most clearly

indicated is the prevention of its photochemical decomposition by suitable screening."

These results have a very definite bearing on the problem of the industrial production of vitamin-D. Anything approaching a satisfactory yield in the reaction

$$\text{Ergosterol} \xrightarrow{\text{u.v. light}} \text{Vitamin-D}$$

requires prolonged irradiation — an expensive process. Screening a quartz-mercury vapour lamp with vitaglass is obviously wasteful, since the large energy emission of the $265\mu\mu$ and $253{\cdot}6\mu\mu$ (resonance) lines is detrimental to the stability of vitamin-D, and must not have access to the solution undergoing irradiation. It would seem, therefore, as if the mercury vapour lamp is unsuitable for this particular photochemical reaction.

The alternative light sources are carbon or metal arcs. It is quite feasible to obtain suitably treated carbon arcs with little or no emission on the ultra-violet side of $270\mu\mu$. On the other hand, there can be little doubt that the working cost of mercury vapour lamps is lower than that of carbon or tungsten arcs producing the same intensity of ultra-violet light, considering all wave-lengths. These considerations prove that the photochemical formation of vitamin-D in good yield presents a formidable problem both to research and to costing. There seems, however, every reason to expect a solution if the experiments are accurately controlled by spectroscopic means.*

The experience of biochemists on the irradiation problem indicates that ergosterol must occur to some extent in a very large and varied number of materials. The fact that ergosterol has hitherto only been found in ergot and yeast fat by no means proves that these are the best sources, and since medical experience indicates a wide field of

* The subject has recently been further discussed in the following papers: Vitamin-D, I. Activation of cholesterol: A. Jendrassik and A. G. Keményffi (*Biochem. Z.*, 1927, **189**, 180). Photo-chemical production of vitamin-D from ergosterol: Rosenheim and Webster (*Lancet*, 1927, ii. 622). Absorption bands of ergosterol and vitamin-D: Heilbron, Kamm, and Morton (*Nature*, 1927, **120**, 617). Absorption Spectra of some Cholesterol Derivatives: Heilbron, Morton, and Sexton (*J.C.S.*, 1928, 47).

usefulness of vitamin-D, a protracted search for the best and cheapest method of preparation would seem to be justified.

A step in this direction has been taken by Heilbron, Kamm, and Morton (*Biochem. J.*, 1927, **21,** 1279) in a survey of the absorption spectra of vegetable oils with reference to the detection of the ergosterol bands. These authors first satisfied themselves that the ordinary constituents of vegetable oils—glycerides of fatty acids, free fatty acids,

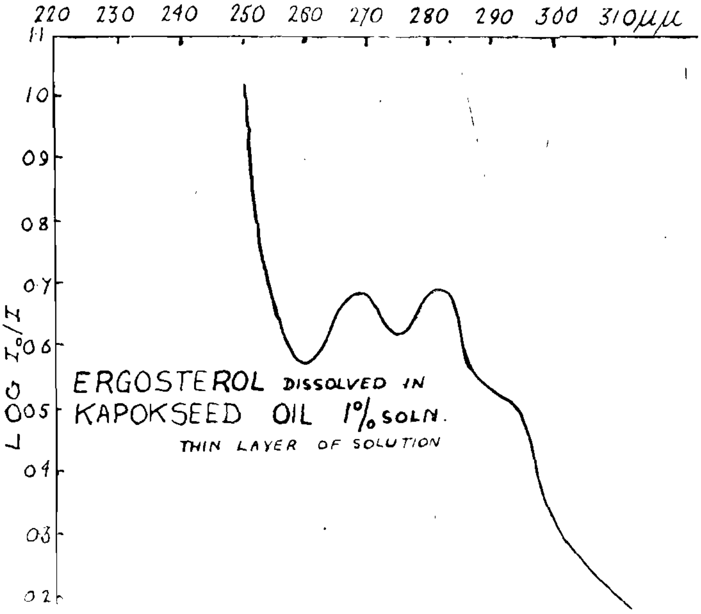


FIG. 29.

phytosterols, etc.—were not as a rule likely to interfere seriously with the optical tests. They then selected a very transparent oil in kapok-seed oil, which showed no signs of selective absorption, and then by adding a small amount of ergosterol proved that the bands would show up in the oily medium.

A large number of oils and other preparations relevant to the egosterol question were examined spectroscopically and the results are summarised in the following table.

ERGOSTEROL IN OILS

Oil.	Ergosterol bands.	Band at or near 320μμ.	Remarks.
Olive (free from adulteration)	—	—	Band at λ max. =407μμ
Nux vomica ..	—	—	
Tiger nut	—	—	
Alfalfa seed	Very feeble	—	
Coconut	—	—	
Babassu	—	—	
Yeast fat	++++++	—	
Sesame	?	—	Well-defined band λ max.=287μμ
Kapok seed	—	—	
Rape	—	—	
Soya bean	—	—	
Mowra seed	Inflexion 265–280μμ	—	
Illipe nut	?	—	Selective abs. λ max. =270μμ
Shea nut	?	—	Selective abs. λ max. =278μμ
Cotton seed	++	—	
Linseed	++	—	
Maize	++	—	
Ground nut—			
Sample A. ..	Inflexion	—	
,, B. ..	—	—	
,, C. ..	—	—	
,, D. ..	+	—	
,, E. ..	+	—	
,, F... ..	++	+	
,, G. ..	++	++ λ max. =319μμ	
,, H. ..	++	++	
Brazil nut	—	—	
Palm oil	—	—	
Palm kernel	—	—	
Rice meal	—	—	
Pumpkin seed ..	?	—	Well-defined selective absorption λ max. =276·5μμ
Whale	—	?	No fine structure
Wool fat	Inflexion	++	
Cod-liver oil	?	+	
Do. unsap.	?	+	
Ostelin	?	+	
Extracted cod-liver oil	?	++	

Certain of these oils will now be discussed in more detail.

Cotton-seed Oil.—This showed the ergosterol bands

plainly (Fig. 30). The unsaponifiable matter obtained by the usual method of saponification of a large quantity of oil gave a high yield of crystalline sterol, which was fractionally crystallised from ethyl acetate, the various fractions then being examined spectroscopically. The

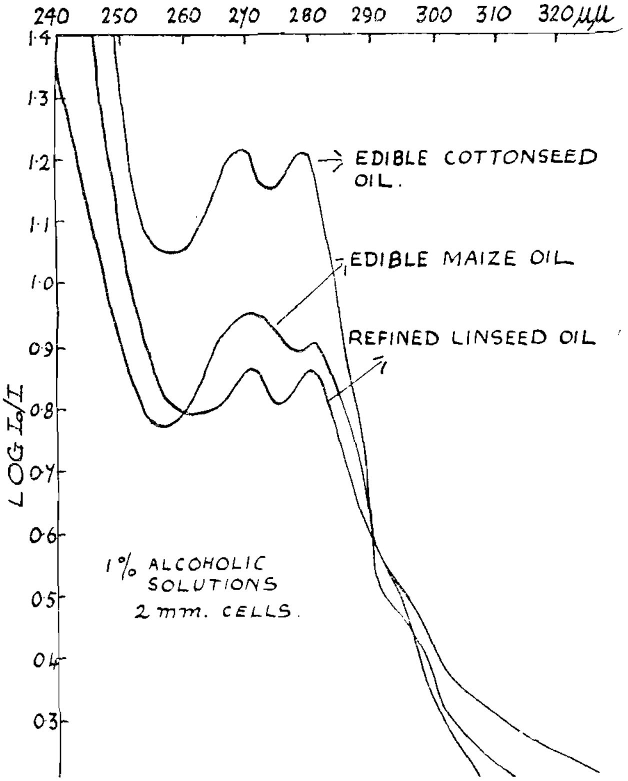


Fig. 30.

least soluble fraction was found to contain 2·5 per cent. the most soluble 0·75 per cent. of ergosterol.

Cotton-seed oil would thus appear to be a very rich source of this compound.

Sesame, Illipe Nut, Shea Nut, and Pumpkin-seed Oils.—These all show well-defined selective absorption in the middle ultia-violet. Since, however, these bands do not

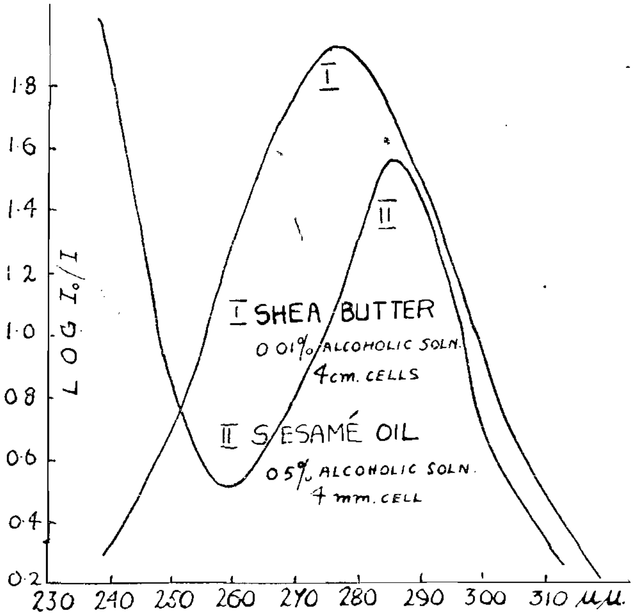
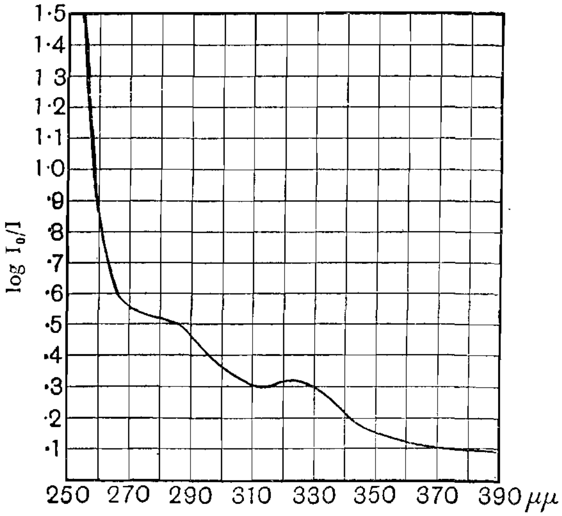


FIG. 31.



Cambridge University Press.] [*Biochemical Journal*.

FIG. 32.—Cod-liver oil film, approx $\frac{1}{10}$ mm. thickness.

exhibit the fine structure characteristic of ergosterol, there is no valid reason for connecting them with the pro-vitamin.

Moreover, a preliminary examination of the unsaponifiable matter of shea-nut oil gives no indication of the presence of ergosterol.

Yeast Fat.—As would be expected from the work of MacLean and Thomas, who found it to contain as much as 40 per cent. of ergosterol, this fat gave by far the most pronounced absorption of all the oils examined.

Ground-nut Oil.—This was probably the most interesting

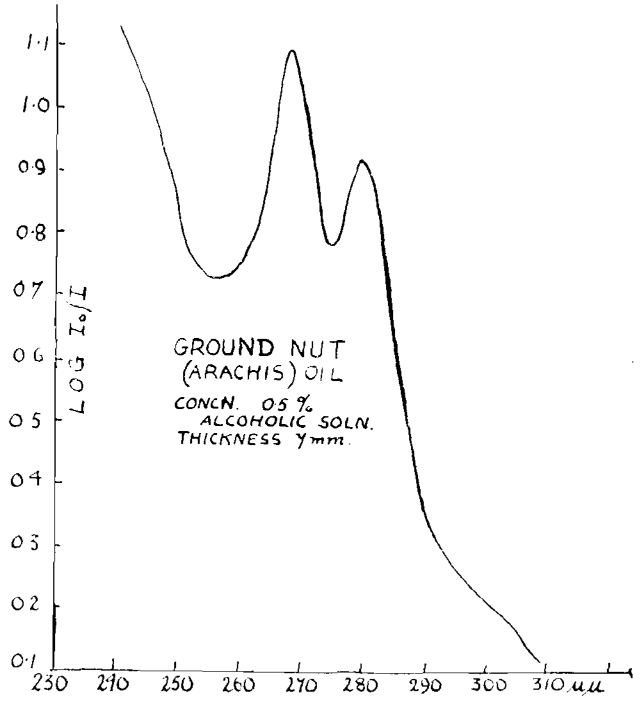


FIG. 33.

oil examined, showing, as it did, big variations from sample to sam e. In some cases there was no sign of selective absorption, in others very well-defined ergosterol bands were obtained. Moreover, in all cases where there was also a more or less

well-defined band in the neighbourhood of $320\mu\mu$. This latter band has only been found hitherto in oils of animal origin, such as wool fat, whale oil, cod-liver oil, etc. (*cf.* Schlutz and Morse [15]; Heilbron, Kamm, and Morton [16]), and there is no definite evidence of its connection with vitamin chemistry.

In concluding this account of vitamin-D some reference should be made to its mode of operation in the body. Beyond the fact that most of the diseases cured by light-therapy are associated with defective metabolism of calcium and phosphorus, *e.g.* rickets, surgical tuberculosis, and that vitamin-D exerts a very similar effect, we know little of the chemistry of the vitamin.

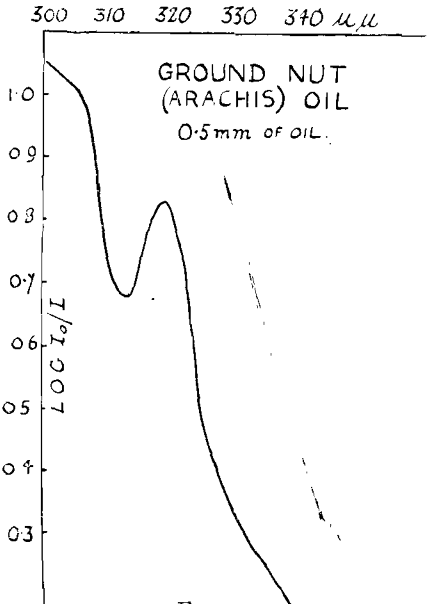


FIG. 34.

The very direct connection between vitamin-D, light, and calcium metabolism is confirmed in an interesting manner by the fact that the administration of cod-liver oil and calcium lactate mixtures causes totally different effects from the administration of either alone. Another observation which supports these views is that abnormal quantities of calcium or sodium salts in the skin cause greater susceptibility of the skin to erythema, and in the eye they increase the effectiveness of ultra-violet radiation in producing cataract.

The case therefore seems to be complete for associating:

calcium metabolism;
cure of rickets, sunlight or cod-liver oil;
activation of foodstuffs.

Hart, Steenbock, and Elvejem[20] record that ultra-violet radiation influences the storage of calcium and of phosphorus in lactating animals, and enables them to assimilate as much as they secrete in the form of milk, thus redressing a negative balance of bone-forming materials. No apology is therefore needed for dealing in some detail with the influence of artificial ultra-violet rays on the nutrition of farm stock, as the industry of producing supplementary rations in the form of cattle and other foods is directly connected with chemistry.

A very valuable paper on this subject has recently been published by Orr, Henderson, and Crichton.[21] Young pigs about nine weeks old were subjected to light treatment from a carbon arc at a distance of three feet for one hour daily. As a result, the amount of calcium and phosphorus which the pig was able to retain in its body was markedly increased, and the amounts excreted in the fæces were correspondingly diminished. In this experiment the ratio of calcium to phosphorus in the diet was 1 : 2, whereas in sows' milk the ratio is 1 : 1. If the young pigs received a more correctly balanced diet the effect of ultra-violet irradiation was less pronounced. The extraordinary rapidity with which young pigs grow entails an increased liability to the breakdown of calcium and phosphorus metabolism and the development of rickets. The authors suggest the advisability of irradiation for pig breeding.

The next experiments were carried out on lactating goats. During the period of lactation the milking cow is generally losing from her body more calcium and phosphorus than she is capable of ingesting from a normal ration, and the drain on her store of these elements impoverishes the skeleton. In one test a lactating goat was able to convert a negative calcium balance into a positive balance when she was subjected to daily irradiation. Actually, then, the light enabled her to increase her resources even whilst lactating.

Young chickens suffer frequently from leg weakness—a condition akin to rickets. Very satisfactory results have

been obtained by irradiation. During the laying season the mineral requirements of hens are very large, and it has been shown by Hughes and Payne [22] that ultra-violet light increases :

(1) egg production ;
(2) hatchability ;
(3) percentage calcium in the shell ; and
(4) percentage calcium in the egg.

Hart and his co-workers found that a group of hens treated with ultra-violet light continued to lay abundantly, while a corresponding group which was untreated, fell off in egg production almost to the zero point. In the former case the hatchability remained at 60 per cent., while in non-irradiated hens it fell to zero.

The conclusions of the Scottish workers are worth quoting : "Farm animals, with their enormous capacity for transforming food which is of little direct use to human beings into products of the highest nutritional value, are particularly prone to diseases of malnutrition. While it must be admitted that against such the first line of defence is an adequate and well-balanced diet, ultra-violet light has been shown to be a most valuable adjuvant. Its effects are most marked in those conditions in which there is a strain on the calcium and phosphorus metabolism. Examples of such are growth, rickets, pregnancy, lactation, laying. It is suggested that there should be a fuller utilisation of sunshine for farm animals, and the employment of artificial means of irradiation in winter is put forward as worthy of trial. The agriculturist should realise that the beneficial influence of sunshine falls not alone upon his crop but on all farm animals. There is thus in nature a 'calcium cycle' comparable to the better known 'nitrogen cycle.' In the latter a seemingly extraneous but all important factor is the intervention of bacterial action. A corresponding part is played by ultra-violet light in the calcium cycle."

The importance of this work for chemists lies, of course, in the now well-established fact that foodstuffs can be rendered anti-rachitic by irradiation. It seems highly

probable that the *sterols* of the type of ergosterol will be capable of isolation cheaply and abundantly from vegetable oils. Ergosterol on irradiation acquires literally enormous anti-rachitic activity, and manufacturers of patent cattle foods and special meals, etc., of all kinds will be well advised to follow the progress of research in this field. Direct irradiation of farm stock is not without considerable difficulties, apart from the fact that the majority of farms are still without the necessary electrical supply.

Foods inoculated with minute quantities of irradiated ergosterol will probably succeed in providing the stock with the necessary regulating mechanism for correct calcium and phosphorus metabolism. It must be emphasised that we are not concerned with curing disease so much as prophylaxis, and that the object aimed at is not what we now associate with "normal" production or "normal" health, but the maintaining of supernormal activity, *e.g.* in egg laying, lactation, etc.

The industries dependent on milk should benefit, and even large expenditure on research and experiment is not in the least likely to be wasted. It would be difficult to over-estimate the value of good milk of potent vitamin activity in the months of late winter and early spring.

Sheard and Higgins [23] have studied the effect of general and selective irradiation by means of a quartz-mercury vapour lamp on the germination and growth of seeds. Filters were used to screen out by stages the various regions of the ultra-violet. An air-cooled lamp was used, which brought about a permanent erythema in 6 minutes at 50 cm.

It was found that selective irradiation modified the time of germination and the rate of subsequent growth. The region 320–390$\mu\mu$ is particularly effective for inducing growth, whilst from 270 to 320$\mu\mu$ the reverse effect is observed. It is interesting that the latter region is noted for the effect of light therapy. The experience of these authors supports the view that the near ultra-violet region aids germination and growth or the "normal functioning of an organism" kept in an unphysiologic environment.

The visible region is regarded as assisting exogeneous metabolic processes. Seeds which normally germinate and grow underground thrive best without irradiation of any kind. Indeed the expression

$$L = k \cdot \frac{1}{\log nt}$$

(L being the growth, t the daily period of irradiation, and n the number of days)

is given as according with the experimental observations. The worst results were obtained with seedlings subjected to diffuse daylight under glass. In this case ultra-violet irradiation brought about an accelerated germination.

A protracted study of the effect of ultra-violet rays on the germination and early growth of plants has been carried out by Popp, and a précis of the works is found in the shape of a private communication to Ellis and Wells (*Chemical Action of Ultra-violet Rays*).

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Ellis and Wells, in their *Chemical Action of Ultra-violet Rays*, give a detailed account of the state of the subject in 1925.

Section VIII.—APPLICATION OF X-RAYS

Whenever rapidly-moving electrons hit matter, X-radiation is generated. The X-ray tube is merely a device for securing collisions of this type, and the complications of design which have appeared in recent years are all directed towards making the impact between electrons and matter more severe, more easily controllable, and more effective in producing high intensities of X-radiation of different types.

The early X-ray tubes consisted essentially of two metal electrodes mounted in a glass tube. The pressure in the tube was reduced to a fraction of a millimetre and the electrodes connected to a source of high-tension current. In this way electrons were projected from the cathode, to impinge upon the surface of a metallic target or anti-cathode placed at a suitable position in the trajectory.

Tubes of this simple kind are called "gas tubes." They suffer from disadvantages due to the necessary presence of residual gas, and their performance is impaired by changes in pressure during operation. At the present time Coolidge or Lilienfeld tubes are more commonly used. In these types the degree of evacuation is made as high as possible, and the flow of electrons is regulated by the temperature of an electrically heated wire acting as cathode. This may be of tungsten or may be covered with a layer of oxides of the alkali earth metals.

The metal for the anti-cathode or target must be carefully chosen. It must possess the following properties:

(1) High melting-point, high thermal conductivity, high specific heat.
(2) High atomic weight.
(3) Low vapour pressure.

For radiography and for purposes requiring white X-radiation (*e.g.* Läue photography) tungsten is probably the most suitable metal, whilst for work in which monochromatic X-rays are desired (*e.g.* rotation and ionisation experiments) molybdenum is probably best except for work involving high dispersion, when iron and copper are recommended. The gas tube (Fig. 35) must contain an appreciable amount of residual gas. The motions of the ions are accelerated by the electric field, and the positive ions striking the cathode release electrons. These tend to

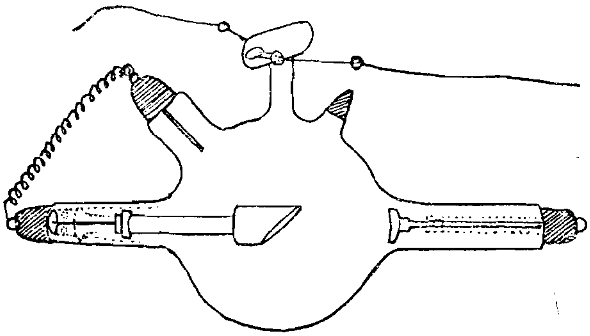


FIG. 35.

flow towards the anode, but many of them collide with particles of the residual gas and in so doing effect further ionisation. The process rapidly increases in efficiency, and in a very short time X-rays are being generated freely at the anti-cathode as a result of electron impacts. The deterioration of gas tubes is due to a decrease in the pressure of the residual gas. Positively charged atoms of gas strike the glass walls with such velocity that they penetrate sufficiently far to be mechanically retained or " imbedded " in the glass. Such atoms are removed from the sphere of action and the pressure in the tube decreases.

In the Coolidge tube a spiral of tungsten wire is mounted inside a cup of molybdenum (see Fig. 36). The pressure within the tube is very low, probably not more than 5 per cent. of that occurring in an ordinary gas tube. In order to maintain such a high vacuum during the

period over which the tube is used it is essential that all the electrodes should be thoroughly "out-gassed." Nearly all metallic specimens contain appreciable quantities of occluded gas, which can only be driven off by strong heating. Accordingly, electrodes intended for Coolidge tubes are subjected to intense preheating. Fortunately, once they are out-gassed the metals do not take up gas with any great avidity; so that it is not necessary to complete the manufacture of the tube immediately after driving off occluded gas. It is not even necessary to repeat the out-gassing process in repairing a broken Coolidge tube. In some of the many different Coolidge tubes now available the tungsten

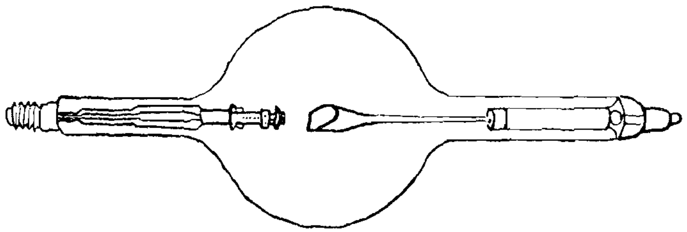


FIG. 36.

target is mounted in copper, and the whole massive piece of metal is kept cool either by a system of vanes (a metallic radiator) or by a current of water. The performance of the "hot cathode" or Coolidge tube depends:

(*a*) upon the number of electrons emitted, *i.e.* the temperature of the heated tungsten spiral; and

(*b*) upon the voltage.

The current and the voltage can be varied independently in the Coolidge tube, whereas in the gas tube the current increases with the voltage. The Coolidge tube is capable of precise control, and definite conditions of X-ray output can be accurately reproduced. This advantage over the gas tube has to be set against the fact that very high voltages are employed more efficiently in the gas tube.

The Lilienfeld tube acts as a combination of the hot-cathode tube and the gas tube. It is said to possess the advantages of both. Very successful all-metal tubes

have been described by Shearer, Siegbahn, Westgren and Phragmen, and others.

At the beginning of the present century the exact nature of X-rays remained in doubt. If they were electro-magnetic vibrations undulatory like light, the phenomena on which the wave theory of radiation was based should be exhibited by X-rays. Refraction at the surface of separation of two media and diffraction fringes had not at that time been observed with the Röntgen rays. The unsuccessful attempts to observe these phenomena had, however, established one important fact, namely, that if the X-rays were ether vibrations, their wave-lengths were bound to be very much smaller than the shortest ultra-violet rays then known to science. The order of the wave-length of light is 10^{-5} cm., whilst for the Röntgen rays the negative results ruled out wave-lengths much greater than 10^{-8} cm. It turned out that the nature of X-rays was to be established by the confluence of two streams of thought—physical and crystallographic theory. The intellectual background of crystallography had been profoundly influenced by Häuy's assumption that crystals should be made up of little elements distributed over a three-dimensional space lattice. Bravais and Frankenheim had demonstrated geometrically the nature and number of the different lattice types, whilst Sohncke, Schoenfliess, and others had determined the space groups capable of existence. Finally, the physico-chemical magnitude known as the Avogadro number (absolute number of molecules contained in one gram-molecule) fixed the order of magnitude of the crystal units as 10^{-8} cm. The background of physics, on the other hand, was such that an unequivocal demonstration of the undulatory nature of X-rays needed to be in terms of refraction or diffraction.

Now, if a beam of ordinary white light, after passing through a slit and collimator, is allowed to traverse a glass plate bearing a series of very closely ruled parallel straight lines, the image of the slit obtained on a screen placed behind the "grating" consists of a central line and a diffraction

pattern showing the resolution of the white light into its component colours. The light has been deviated by an amount depending on its wave-length. In order to obtain this phenomenon the grating space d (distance between successive lines) must not exceed $\lambda/2$, where λ is the wave-length of the light used.

In 1912 M. v. Läue suggested that the "grating space" of crystals would fit the wave-lengths of X-rays. The crystalline grating would, however, differ from the grating ruled on glass, since the latter is on a plane and is periodic in one dimension only, whereas the former is built in space and is periodic in three dimensions. Läue studied the idea theoretically and predicted what would happen if a beam of "white" (complex) X-radiation were allowed to traverse a three-dimensional lattice. He calculated that the X-rays would be focussed in spots in a manner corresponding with the orientation and symmetry of the diffracting lattice. Friedrich and Knipping carried out the experiment suggested by Läue. They allowed a parallel beam of X-radiation to traverse a crystal of rock-salt, blende, or diamond, so that the emergent rays would strike a photographic plate. After several hours' exposure they obtained the predicted spots or Läue pattern, as it is now called. This was one of the most significant of experiments, because the successful realisation of Läue's idea, established at one and the same time the nature of X-rays, and the space lattice theory of crystal structure.

The preparation of Läue photographs is illustrated in Fig. 37. The symmetry of the crystal is shown by the symmetrical grouping of the spots.

The best Läue photographs are obtained with an X-ray tube running at 50–60 kilovolts * and an anti-cathode of tungsten, because this metal gives the nearest approach to "white" X-rays, *i.e.* X-rays showing a continuous spectrum. An exposure of 15 milliampère hours is usually about right.

* This voltage is chosen because the peak corresponds with the absorption limits of the silver in the photographic plate.

The interpretation of Läue photographs is often very complicated. It is nowadays usual to determine the length of the unit cell by another method ; given this constant the Läue pattern is still a very useful weapon for research.

The determination of the length of the unit cell depends on the use of Bragg's X-ray spectrometer.

Consider a crystal prepared so that one of its surfaces is parallel to a set of parallel planes separated by a distance d.

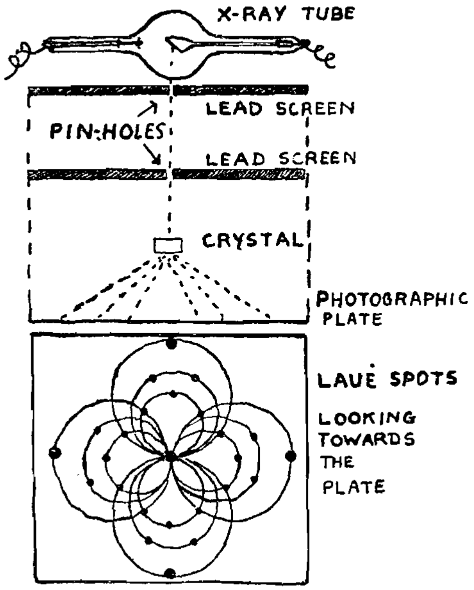


FIG. 37.

Now, let a beam of monochromatic X-radiation of known wave-length strike the crystal surface (Fig. 38). A reflection BC occurs when the diffracted wave from B is reinforced by the waves reflected from B′, B″, B‴, etc. The laws of diffraction show that this can only occur when the distances AB, A′B′+B′B, A″B″+B″B, etc., differ by an integral number of wave-lengths. On this basis it is clear that :

$$\lambda = 2d \sin \theta_1$$
$$2\lambda = 2d \sin \theta_2$$
$$3\lambda = 2d \sin \theta_3$$

d being the distance between successive planes. The angles θ_1, θ_2, θ_3 are called respectively angles of 1st, 2nd, and 3rd order reflection; λ is, as will be shown, a known quantity, so that d can be calculated if θ_1, θ_2, θ_3, etc., can be measured.

By determining these angles for various planes in crystals, W. H. Bragg and W. L. Bragg have elucidated the architecture of many crystals, and the results are already classical.

The experimental method may be very briefly described. An X-ray tube can be obtained which is only emitting certain very nearly monochromatic radiations characteristic of the anti-cathode metal, which is usually rhodium or molybdenum. The apparatus is described as an X-ray spectrometer. It

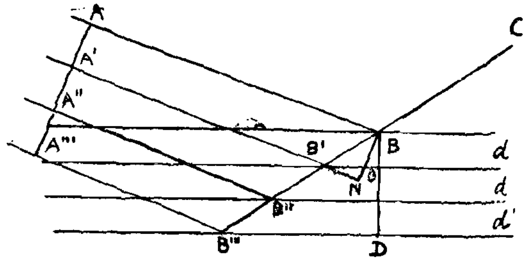


FIG. 38.

consists of one or more slits to yield a fine pencil of X-rays, a table upon which a crystal may be mounted at any desired angle, and finally an ionisation chamber for measuring the intensities of rays reflected from the crystal face. A typical ionisation chamber consists of a brass cylinder 16 cm. × 5·5 cm., fitted with a "window" of mica or aluminium foil. A brass rod runs along the length of the tube, and its position is adjusted so that it is just out of the direct path of the rays entering the cylinder. The rod is insulated by means of sulphur, and is connected to an electroscope by means of a wire passing through an earthed shield. The ionisation chamber is practically air-free, and contains a heavy vapour such as methyl iodide, methyl bromide, or sulphur dioxide. The ionisation is due only in

part to the X-rays themselves, since the secondary particles detached from the vapour molecules are also very effective. The current which flows as a result of this ionisation causes a change in potential, which is indicated by the electroscope and provides a measure of the intensity of X-rays entering the ionisation chamber.

It is of interest that methyl bromide, which liquefies

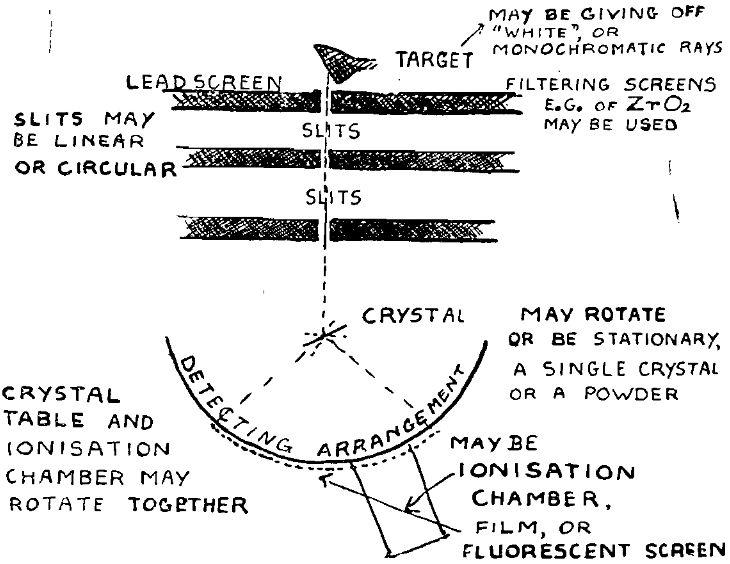


FIG. 39.

Diagrammatic representation of methods for the investigation of crystal structure by means of X-rays.

at 4·5°, can be kept without danger in sealed bottles at room temperature.

One way of using a spectrometer is to have the rotating table, upon which the crystal is mounted, fastened to the ionisation chamber, so that the angular velocity of the latter will be twice that of the former. By this device the reflected rays will always enter the chamber after a correct initial setting. By carrying out a series of ionisation measurements the entire range of reflections characteristic

of a crystal plane may be explored. This method is convenient for a preliminary survey. In order to ascertain the relative intensities of the different reflections the crystal table and the chamber are allowed to move independently. The chamber is first fixed in such a position that a given reflection is recorded with maximum intensity. The crystal is then carefully rotated about a position θ, if 2θ is the angle at which the ionisation chamber is adjusted. Numerous observations of intensities at angles a little $\gtrless \theta$ are carried out, and the result is expressed by plotting the angular position against the recorded intensity.

The X-ray spectrometer has numerous disadvantages, and Wyckoff goes so far as to say that "the uncertainty concerning the accuracy of the existing spectrometer observations, combined with the theoretical limitations to their use, make them the least reliable of all crystal structure data." It is, however, true to state that all of the difficulties may be surmounted if sufficient care is taken.

If the distance from the slit to the crystal is equal to that separating the crystal and the detecting arrangement, X-rays of a definite wave-length will always be brought to a focus at the detector, even when the original beam is quite divergent. This fact is important for both photographic and ionisation methods.

By replacing the chamber with a photographic plate a limited X-ray spectrum can be recorded. Unless the crystal is an unusually fine specimen the spectrum is distorted, but M. de Broglie[1] (*Compt. rend.*, 1913, **155,** 924) found that by rotating the crystal backwards and forwards during the exposure very much superior results could be obtained.

As might be expected, the construction of X-ray spectrographs has developed in many directions and exceedingly beautiful and complicated types of apparatus are now available. It must, however, suffice to refer those interested to the book published by Siegbahn.

The Powder Method.—Instead of a face from a single crystal, it is possible to use a thin film of crystalline powder.

The tiny crystals will be randomly oriented, and all the separate reflections of all orders from every possible atomic plane will reach the photographic plate, and the resultant diffraction pattern will indicate the important planes. The powder method works effectively only with monochromatic X-rays, as otherwise the interpretation of the photographs would prove too formidable a problem. The method is associated with the names of Debye and Scherrer [2] (*Physikal. Z.*, 1916, **17**, 277) and Hull [3] (*Phys. Rev.*, 1917, **10**, 661).

The powder should pass through a 250-mesh screen and the X-rays should be filtered to secure monochromatism. Exposures are necessarily rather lengthy, but this factor is of small consequence compared with the vast possibilities of a method capable of elucidating the fine structure of solids which do not form large crystals. X-rays from the target pass through a series of slits, impinge on the powder, and are diffracted and recorded upon the photographic film mounted semicircularly.

The powder is mounted on a thin rod or film on the axis of a cylinder, and if the slits are pinholes the pattern is a series of curved bands, whilst if line slits are used it consists of lines which are practically straight and parallel, and are therefore suitable for accurate work. The powder method has been enormously used in recent years, and a noteworthy feature is the growing use of simultaneous exposures with a number of cameras, as many as twenty-four having been used at once.

Interpretation of X-ray Data.—The relation $n\lambda = 2d \sin \theta$, deduced by W. H. and W. L. Bragg, makes it possible by measuring θ to calculate either d or λ if the other is known.

The equation shows that a beam of complex radiation striking a crystalline face characterised by a "grating space" d will be reflected in different directions, depending on the magnitude of the different wave-lengths. The result will be a "dispersion" similar to the resolution of the components of white light into a spectrum. If monochro-

matic X-rays can be obtained the measurement of θ for different crystal planes will give the distances between successive like planes. In this way all the parameters of the unit can be evaluated *relatively* and a model envisaged. The *absolute* dimensions of the unit cell will depend on the absolute value of the monochromatic X-radiation.

We must now digress and consider the production of monochromatic rays. When X-rays strike a substance two effects occur:

(*a*) The production of radiation of very nearly the same hardness or penetrating power as the incident radiation. This effect is independent of the nature of the substance. It is termed "scattered radiation," and its nature is best realised by regarding it as analogous to the light scattered from a piece of white paper.

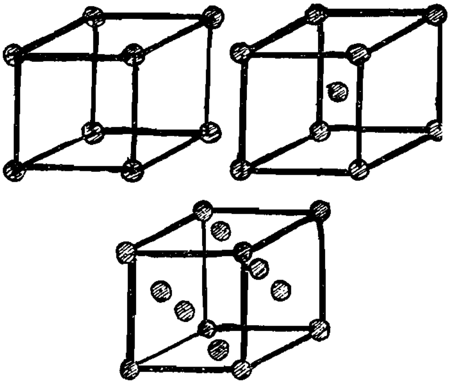
(*b*) The production of rays the penetrating power of which depends on the chemical nature of the substance bombarded. This radiation is always excited by radiation harder than itself (just as fluorescent light is always longer in wave-length than the exciting light—Stokes' law (see p. 167)). The X-rays excited are peculiar to the substance in the same way as the D-spectral doublet is characteristic of sodium.

Both (*a*) and (*b*) can be excited by the impact of swiftly-moving electrons.

Barkla subdivided the characteristic X-rays into two homogeneous beams and called them the K- and L-rays of the element bombarded, and Moseley later used a crystal as a reflection grating to show that the K-radiation could be resolved into sharp spectral lines. From this work he developed the conception of Atomic Number. It is clear that there is no particular difficulty in securing monochromatic X-rays of a suitable wave-length now that X-ray spectra are known. We have, however, still to explain how an absolute determinaton of X-ray wave-length can be carried out. Either d or λ in the Bragg equation must be obtained.

Three cubic lattices are possible :

Simple cubic lattice. Body-centred lattice.



Face-centred cubic lattice.

FIG. 40.

It can be shown that in the lattices :

$d_{100}=a$, $d_{110}=a/\sqrt{2}$, $d_{111}=a/\sqrt{3}$ for a simple
$d_{100}=a$, $d_{110}=a\ \sqrt{2}$, $d_{111}=a/\sqrt{3}$ for a body-centred cube,
$d_{100}=a$, $d_{110}=a/\sqrt{2}$, $d_{111}=2a/\sqrt{3}$ for a face-centred cube.

In the case of potassium chloride the experimental results correspond with a simple cubic lattice. With rock-salt, however, it is concluded that the metal atoms alternate with chlorine atoms along the edges of the network of tiny cubes, and that considering only like atoms we obtain in each case a face-centred cubic lattice (Fig. 41). The diffracting power is greater for atoms of greater atomic weight. This result corresponds with two interpenetrating face-centred lattices.

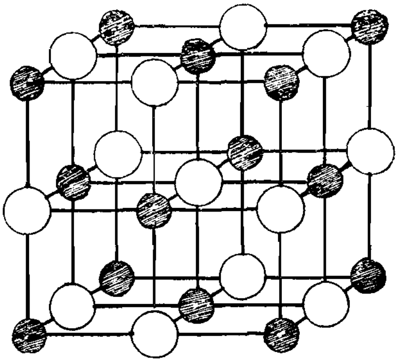


FIG. 41.

In the above diagram there are eight small cubes. The

central atom is an integral part of each cube, *i.e.* there is really one atom per cube. In other words, each elementary cube is associated with half a molecule of sodium chloride.

If Mm is the weight of a molecule of sodium chloride expressed as a multiple of the weight of an atom of hydrogen in absolute units, the weight of an elementary cube will be $\frac{1}{2}$Mm.

This mass is also equal to ρd^3, where ρ is the density of the crystal, and d is the side of the elementary cube, hence

$$\tfrac{1}{2}Mm=\rho d^3$$

$$\therefore\ d^3=\frac{Mm}{2\rho}$$

$$\therefore\ d=\left(\frac{Mm}{2\rho}\right)^{\frac{1}{3}}$$

m may be obtained from the Avogadro number and ρ is known.

For sodium chloride $d=2{\cdot}814\times10^{-8}$ cm.
and for calcite $d=3{\cdot}0283\times10^{-8}$ cm.

If d is known for one crystal, the corresponding values for other crystals may be obtained by comparing the dispersion of the same radiation,

$$i.e.\ d\sin\theta=d'\sin\theta'.$$

Hull showed that chromium, manganese, tungsten, molybdenum, tantalum, and α-iron showed body-centred cubic lattices, but the dimensions of the unit cubes differed from metal to metal. Face-centred cubic lattices were shown by α-cobalt, nickel, rhodium, palladium, indium, platinum, copper, gold, silver, aluminium, whilst β-cobalt zinc, cadmium and ruthenium, exhibit hexagonal prismatic lattices.

A useful way of checking the results is possible if the type of lattice and the number of atoms per unit cell have been determined. Consider a gram-atomic weight of a metal, say iron 56. It will contain N atoms where N is the Avogadro number. The lattice is cubic of side length d and volume d^3, and each unit cube contains x atoms.

If x atoms occupy a volume d^3, N atoms will occupy $\frac{Nd^3}{x}$.

The density will therefore be given by

$$\sigma = \frac{\text{Atomic weight . number of atoms per unit cell}}{\text{Avogadro number . } d^3}$$

$$i.e. \quad \sigma = \frac{\text{At.Wt . x}}{\text{N . } d^3}$$

$$or \quad x = \frac{\text{N . } d^3\sigma}{\text{At.Wt.}}$$

On account of the vast amount of data now available it is impossible even briefly to review the whole field of the X-ray analysis of crystal structure. It is therefore proposed, to select a few typical researches of industrial significance to illustrate the possibilities of the new field of investigation.

The first subject will be the allotropy of iron, and it will be necessary to recall some of the more important facts, for although they may not be directly relevant, it is impossible to show the importance of the X-ray work without fitting it into its proper background.

On heating iron a marked absorption of heat occurs at certain temperatures, and on cooling a corresponding evolution of heat is observed. In certain steels the evolution is so intense that an actual rise in temperature is observed at certain points, so that the phenomenon has received the name recalescence. If the time per unit rise or fall of temperature is plotted against temperature, the curve shows marked discontinuities. Some, at any rate, of these correspond with "allotropic" modifications designated as α-, β-, γ-, δ-iron.

What exactly do we mean by the term "allotropy"? It has been suggested that a crystallographic change at the transformation temperature constitutes a sound criterion of allotropy. On the other hand, a change in magnetic properties has been denied validity as a criterion. Again, it has been maintained that the existence of transformation points is sufficient evidence of allotropic change if heat is absorbed or evolved. The connotation of the term allotropy is thus not too certain.

If we return to the case of iron, we find that the French metallurgist Osmond[4] (*J. Iron & Steel Inst.*, 1890) recorded two thermal transformation points at 760° and 900°, and concluded that above 900° iron existed as a form labelled γ-, between 760° and 900° as β-iron, and below 760° he described it as α-iron.

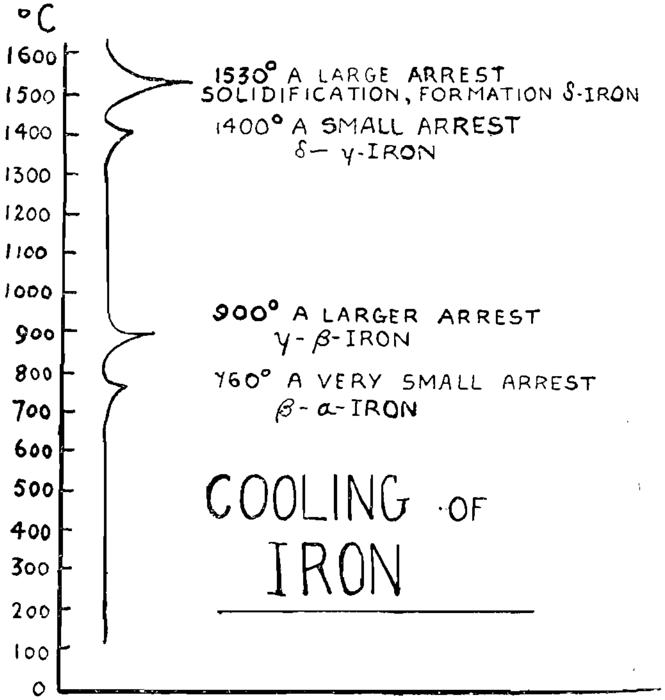


FIG. 42.

The α- and γ-irons are now accepted as true allotropes, but there is still considerable divergence of opinion as to whether the α- and β-irons are really distinct allotropic forms, in spite of the unfailing appearance of the change at 760°. Above 760° iron ceases to be magnetic, but immediately below this point it regains its magnetic properties. If a sudden discontinuity of this kind is a criterion of allotropy, α- and β-iron must be accepted as different modifications. Yet another discontinuity occurs near 1,400°, as will be seen in the figure.

The notation Ac (arret chauffage) and Ar (arret refroidissement) is used for the discontinuities in the heating and cooling curves respectively. Ar_2 means the discontinuity at 760°, Ar_3 that at 898°, etc.

The physical evidence for the allotropy of iron, based on deformation, microscopic structure, dilatation, magnetism, etc., is conflicting, but the X-ray analysis has yielded results of outstanding importance. Westgren and Phragmen [5] (*Jour. Iron and Steel Institute*, 1922, **105**, 241) have determined at different temperatures the space lattice of the purest available iron, and their results seem conclusive.

The X-rays were produced in a Siegbahn tube [6] (*Z. f. Physik*, 1920, **3**, 369; *Z. physikal. Chem.*, 1921, **98**, 181) made of metal, and an anti-cathode of iron was used. Round the anti-cathode were placed five windows, so that with

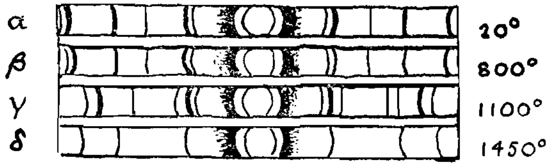


FIG. 43.—X-ray structure of iron.
(Drawn after Westgren and Phragman's photographs.)

five X-ray beams exposures could be made simultaneously with five cameras. The tube was kept exhausted by a mercury vapour jet pump and a mercury diffusion pump. The voltage used was 45,000–50,000 volts, and the current 10–12 milliampères. In the camera, the iron wire was stretched vertically and slowly rotated at the rate of three or four revolutions per minute. It was heated by an alternating current of low voltage, the temperature being determined by a Holborn-Kurlbaum optical pyrometer. The wire consisted of vacuum-melted electrolytic iron (99·98 per cent. Fe) 0·3 mm. in diameter. Photographs were taken of the reflections at 20°, at about 800° C., at 1,100° C., and at 1,425° C., with two hours' exposures. The authors had to overcome many experimental difficulties (see original papers, *loc. cit.*), but we must content ourselves here

with a summary of the results. Iron at room temperature possesses a body-centred cubic lattice (Fig. 43), the side of the unit cube being 2·87 Å. long. Furthermore, α- and δ-iron possess almost identical space lattices. On the other hand, γ-iron exhibits a face-centred cubic lattice, the length of the side of the unit cube being 3·65 Å. The changes occurring at 900° and 1,400° thus involve complete recrystallisation and drastic rearrangement of the atoms. It is scarcely possible any longer to deny that allotropic transformations occur at these temperatures. The condition of iron in the temperature region 760–900° (β-iron) corresponds with a body-centred cubic lattice with a length of 2·90 Å. for the side of the unit cube. The value of this constant is very close to that of α-iron. If a change in crystal structure is essential to allotropy, then the individuality of β-iron as an allotrope may be denied. This does not, of course, explain or dispose of the energy change at 760°.

It is interesting to correlate these results with other properties. For iron at room temperature $a = 2{\cdot}87$ Å., at 800° C. the value is 2·90 Å., and at 1,425° C. it is 2·93 Å. The mean value of the dilatation coefficient of iron is $15 \cdot 10^{-6}$, which agrees well with the above.

The heat expansion of the γ-iron is seen from the increase of a_2 from 3·63 Å. at 1,100° C. to 3·68 Å. at 1,425°. This agrees with the fact that the dilatation coefficient of γ-iron is greater than that of α-iron.

Westgren and Phragmen point out that the reversal of crystal structure at 1,425° C. is not so surprising as it might appear. Weiss and Foex [7] (*Jour. Phys.*, 1911, **1,** 745) plotted magnetic susceptibility against temperature and found that the curve indicated an identical structure for α-, β-, and δ-irons, since the δ-range was a continuation of the α-, β-range with the γ-iron part of the curve entirely removed.

The Iron-Carbon System.—Pure iron is, of course, of little metallurgical importance, but the theoretical knowledge of its allotropy is essential to the understanding of the iron-carbon system, which is of enormous industrial significance.

It is necessary in the first place to explain the terminology in use for describing the constituents of steels. It is largely as a result of research in metallography that the existence of the following substances has been established :

Austenite consists of a solid solution of iron carbide (Fe_3C) in γ-iron. Alloy steels may contain almost 100 per cent. of austenite as octahedral crystals.

Cementite consists of iron carbide, Fe_3C.

Ferrite is free α-iron. It may contain silicon, phosphorus, or manganese in solid solution.

Graphite (free or "graphitic" carbon) appears after annealing in steels very rich in carbon, and also in grey cast iron. It is usually formed by the breakdown of iron carbide.

Martensite is regarded as colloidal, and contains α-iron plus iron carbide. It is the first decomposition product of austenite.

Pearlite is the iron—iron carbide eutectoid. It consists of 21Fe : Fe_3C by weight, or 6·5 Fe : Fe_3C by volume.

Troostite is the second decomposition stage of austenite. Other constituents such as osmondite and sorbite need not be entered into here.

The application of these terms may be illustrated by the changes undergone by a 0·25 per cent. carbon steel, consisting of 25 per cent. pearlite and 75 per cent. ferrite.

720° Ac_1. Pearlite becomes austenite, leaving ferrite as α-iron.

769° Ac_2. Ferrite becomes β-iron, magnetic property disappears.

801° Ac_3. β-iron is completely absorbed into austenite, and the material is now homogeneous.

794° Ar_3. The first crystal of β-ferrite is deposited from austenite.

769° Ar_2. The deposition of β-iron is completed, α-iron begins to form, and the magnetic property returns.

695° Ar_1. α-Ferrite deposition continues until the solid solution left corresponds with the eutectoid composition. At this point the austenite is converted to pearlite.

Sufficient has now been said to show the importance of the work, which will now be mentioned briefly.

Westgren and his colleagues [8] (*Jour. Iron and Steel Inst.*, 1924, **109**, 159) have tackled the question of the structure of cementite (iron carbide). Using Läue's powder and rotating crystal methods, they found that the unit cell is orthorhombic, of dimensions 4·518, 5·069, and 6·736 Å. There are four Fe_3C molecules per unit cell, and from these results, a density of $7{\cdot}68 \pm 0{\cdot}05$ was calculated.

Meteoritic iron carbide, known as cohenite, gave a powder photograph identical with that of cementite. Cohenite is thus orthorhombic and not cubic as was once thought.

The lattice dimensions of austenite increase with increasing carbon content. Although it is a solid solution the carbon atoms do not *replace* iron atoms. The iron atoms occupy the points of the face-centred cubic lattice exclusively, and the carbon atoms are situated in the interstices between the metal atoms.

Heindlhofer [9] (*Physical Rev.*, 1924, 426), however, found that in martensite, carbon atoms appear to *replace* iron atoms in the lattice. In the cases of 0·80 per cent. and 1·31 per cent. carbon steels, the same X-ray lines were found as in pure iron, but they were broader, somewhat displaced, and only one-third as intense. Martensite appears to contain two constituents:

(*a*) A solid solution of carbon in iron, the carbon replacing the iron atom for atom in the lattice; and

(*b*) Finely dispersed cementite.

The hardness of these steels appears to be related to the fine grain of the dispersed cementite and to distortion of the lattice in the solid solution.

The elucidation of the crystal structure of iron and steel has already begun to stimulate research in other directions. Thompson and Millington,[10] for instance (*Jour. Iron and Steel Inst.*, 1924, **109**, 67), in their interesting work on the plastic deformation of α- and γ-iron, state that the "X-ray work of Westgren is the basis on which the authors have endeavoured to build their ideas."

The System Copper-Aluminium.—Copper containing a little aluminium retains its malleability and becomes harder. It takes a fine polish and varies in colour from red to pale yellow, according to the aluminium content. Alloys containing up to 11 per cent. of aluminium are called aluminium bronzes, and are referred to as 1 per cent., 3 per cent. bronzes, etc. The term "aluminium bronze" usually applies to the 10 per cent. alloy.

The system copper-aluminium is somewhat complicated, and for that reason it provides an excellent case for illustrating the value of the X-ray method of investigating alloys. The equilibrium diagram (Fig. 44) shows seven

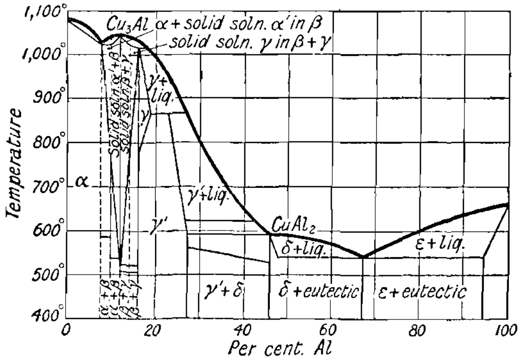


FIG. 44.—Equilibrium diagram of aluminium and copper alloys. (*From J. W. Mellor's "Comprehensive Treatise."*)

solid phases, designated α, α', β, γ, γ', δ, ϵ, all of which are solid solutions. At 9 per cent. aluminium, and 68 per cent. aluminium, minima are shown at 1,038° and 545° respectively. The compound Cu_3Al is indicated by a maximum at 1,050° and at 588°, a somewhat imperfect maximum corresponds with a compound $CuAl_2$.

For the α-phase the solidus and liquidus curves are not very well separated, so that the composition of the portion crystallising first is not very different from that of the material crystallising later. For alloys containing up to 12·5 per cent. of aluminium a complex series of solid solutions is indicated. The precise properties of these solutions vary with the rate of cooling, whilst complete

agreement has not yet been reached as to the effect of annealing at different temperatures.

The system has been studied by means of X-rays by E. C. Bain[11] (*Ind. Eng. Chem.*, 1924, **16,** 692), Owen and Preston[12] (*Proc. Phys. Soc.*, 1923, **36,** 14), Jette, Phragmen, and Westgren[13] (*Inst. Metals*, 1924, **31,** 193), and by Rosenhain,[14] and Becker and Ebert.[15]

A thoroughgoing attack on the problem, especially by the Swedish workers, has resulted in a very trustworthy picture, which may be summarised as follows:

α-phase (0·7 per cent. aluminium). The added metal acts by simple substitution; the copper lattice is retained but enlarged.

γ'-phase (16–25 per cent. aluminium). The crystals show cubic symmetry, the side of the cell being roughly 9 Å. in length. Although aluminium enlarges the copper lattice in the α-phase it contracts it in the γ-phase, *e.g.* d=8·701 Å. (16 per cent.); 8·656 Å. (25 per cent.). It is interesting to note that in the α-phase simple substitution occurs in a cell containing 4 atoms, whilst 49–52 atoms are required for the unit cell of the γ'-phase, formulæ such as $Cu_{27}Al_{22}$, $Cu_{30}Al_{20}$, $Cu_{33}Al_{18}$, $Cu_{36}Al_{16}$ being indicated. The variation of density with proportions of the two metals points to the conclusion that three copper atoms are replaced by two aluminium atoms.

W. T. Astbury and W. H. Bragg[16] (*Ann. Reports Chemical Society*, **21,** p. 223), describe this as "a truly astonishing state of affairs, and its full meaning is at present quite beyond any conjecture."

δ-phase (46 per cent. Al, *i.e.* $CuAl_2$) consists of a body-centred tetragonal lattice, a=6·05 and c=4·88 Å.U., containing four molecules of $CuAl_2$ per unit cell.

It has been shown that the 42 per cent. alloy consists of a mixture of γ' and δ, whilst 55 per cent., 80 per cent., and 95 per cent. alloys exhibit the lattices characteristic of the δ-phase and of aluminium itself. A quenched 12·5 per

cent. alloy gave indications of a phase stable only at rather high temperatures.

The study of the copper-aluminium system has been carried almost as far as experimental difficulties will at present allow; it has yielded results of very great significance for the study of alloys, but the extraordinary γ'-phase remains to be elucidated more fully. The complete solution of the nature of this phase will probably mark a definite step forward in the methods of investigation.

Binary Alloys.—Westgren and Phragmen[17] (*Phil. Mag.*, 1925, **50**, 311) have been led to an important conclusion on the basis of X-ray studies to binary systems. The fundamental difference between solid *chemical compounds* and solid *solutions* is to be found from their reasoning.

In a true chemical compound structurally equivalent atoms are chemically identical, whereas in an ideal solid solution all atoms are structurally equivalent. In alloys an intermediate state of affairs is more usual, namely, solid solutions in chemical compounds. The three systems—copper-zinc, silver-zinc, gold-zinc—have five types of structure in common:

(1) a face-centred cubic structure (α),
(2) the cæsium chloride structure (β),
(3) a cubic lattice with 52 atoms per unit cell (γ),
(4) a close-packed hexagonal lattice (ϵ),
(5) a second closed-packed hexagonal structure with a greater axial ratio (η).

(2) and (3) are probably solid solutions in chemical compounds, whereas (1), (4), and (5) approach to the condition of ideal solid solutions.

There is no need to stress the importance of an accurate knowledge of the structure of brasses in relation to hardness and other properties of industrial significance. Even if no immediate practical advantage accrues, these studies of a fundamental nature constitute a very considerable strengthening of the theoretical foundations upon which the metallurgist builds the superstructure of working hypotheses.

Cold-Working of Metals.—Space does not permit of more than a mention of the fascinating results which have been obtained in the X-ray study of rolled metals. The cold-working of metals effects great changes in their properties, especially in respect of hardness. Part of the effect is due to crystal reorientation in the process. In a true powder photograph *random* orientation obtains, but in a rolled metal a condition of anisotropy is set up as a result of a gliding process along favoured planes. Not only do the crystals appear to split into thin layers which can glide fairly freely, but the thin layers seem further to undergo bending. This involves the difficulty that the stretched and shortened planes are almost in contact, so that small lacunæ should arise. It has been shown experimentally that the surfaces of the glide planes are sometimes puckered to counteract this effect.

This fine-folding or puckering appears to play a definite part in the hardening process.

Miscellaneous.—Hyslop[18] (*Trans. Ceram. Soc.*, 1925, **24,** 402) has examined the X-ray diffraction patterns of clays heated to temperatures ranging from 450–1,450°. In kaolinite the clay breaks down completely at about 600°, forming a silicate, presumably $Al_2O_3 2SiO_2$, which is stable to about 900°. He also found that natural sillimanite and mullite are different. The materials can be identified by this method in fired bodies. G. Shearer[19] (*ibid.* 1924, **23,** 314) has also examined the X-ray spectra of china clay in the presence and absence of alumina. The results are interesting, since they show that mixtures rich in alumina after heating to 1,700° contain a new crystalline constituent.

According to Sachs[20] (*Z. Metallk.*, 1926, **18,** 209), there is no change in lattice structure as a result of the ageing of duralumin. X-ray examination of twisted aluminium crystals shows that the tendency of a metal to recrystallise depends on the distortion of the crystal lattice.

The X-ray spectrograph has been applied to the study of the molecular structure of fatty acids. Shearer[21] can now analyse mixtures of fatty acids with a fair degree of certainty.

Piper, Malkin, and Austin [22] point out, however, that the measurement of crystal spacings can only be used as an aid to chemical identification if great caution is exercised.

X-ray Studies on Cellulose.—X-ray investigation has shown that cellulose is composed of minute crystals below the size visible under the microscope. The same X-ray interference phenomena as are observed with larger crystals are shown by naturally occurring cellulose, which, therefore, consists of aggregates of tiny crystallites. This applies to bast fibres, seed hairs, and other plant tissues, as well as to fibres derived from the animal kingdom.

In many fibres the crystallites are arranged so that one of the crystal axes lies in the fibre axis, in other fibres the crystals have an axis fixed at a definite angle to the fibre axis, whilst in cotton a spiral arrangement makes its appearance.

Cellulose exhibits rhombic symmetry, and Herzog [23] find the following values for the edges of the unit cell :

$$a = 8{\cdot}60 \times 10^{-8} \text{ cm.}$$
$$b = 7{\cdot}78 \times 10^{-8} \text{ cm.}$$
$$c = 10{\cdot}22 \times 10^{-8} \text{ cm.}$$

The volume of the unit cell is thus $684 \cdot 10^{-24}$ cm.

From the relation $$n = \frac{V.N.s}{M}$$

where M = molecular weight $C_6H_{10}O_5 = 162$,
N = Avogadro number $6{\cdot}06 \cdot 10^{23}$,
s = density of cellulose $1{\cdot}51$,
and n = the number of $C_6H_{10}O_5$ groups in the cell, it follows that $n = 3{\cdot}9$.

Within experimental error this indicates that there are four $C_6H_{10}O_5$ groups in the unit cell.

From certain aspects of the work it is concluded that two chemically similar but physically different modifications occur. When cellulose fibres are treated with a strong solution of sodium hydroxide, and the alkali is subsequently washed out, the X-ray diagram is altered to an extent

depending on the degree to which this "mercerisation" process has been carried.

If the unit cells for ordinary and mercerised cellulose are compared:

	Ordinary.	Mercerised.	
a	$8{\cdot}60 \times 10^{-8}$ cm.	$8{\cdot}88 \times 10^{-8}$ cm.	horizontal
b	$7{\cdot}78 \times 10^{-8}$ cm.	$8{\cdot}05 \times 10^{-8}$ cm.	along the
c	$10{\cdot}22 \times 10^{-8}$ cm.	$9{\cdot}88 \times 10^{-8}$ cm.	fibre

it will be seen that a contraction of about 3 per cent. has occurred along the direction of the fibre. The crystallite of untreated cellulose is probably about 117 Å. long and 61 Å. wide.

Ambronn, and also Herzog,[24] state that in the case of cellulose nitrate it is only possible to observe crystal structure if the specimen has been prepared under conditions in which the fibre structure is maintained. If in the preparation of either cellulose nitrate or acetate the material has been dissolved at any stage the X-ray pattern is not manifested. Thus, if solution has not occurred the rhombic lattice is retained without much alteration.

	Cellulose nitrate.	Cellulose acetate.
a	10·1 Å.	9·2 Å.
b	8·6 Å.	7·1 Å.
c	20·8 Å.	9·8 Å.

An interesting sidelight on the mercerisation process is shown by the X-ray diagrams obtained under the following conditions:

Untreated cellulose (A structure) ↗ Cellulose nitrate ↖ Cellulose (A structure)

Untreated cellulose (A structure) ↘ Cellulose acetate ↗ Cellulose (A structure)

Mercerised cellulose (B structure) ↗ Cellulose nitrate ↘ Cellulose hydroxide (B structure)

Mercerised cellulose (B structure) ↘ Cellulose acetate ↗ Cellulose hydroxide (B structure)

The fact that the regeneration of cellulose from the acetate and nitrate of the mercerised product does not give the diagram of untreated cellulose is somewhat astonishing. Herzog resists the temptation to draw conclusions as to whether the change produced by mercerisation is to be interpreted from a "chemical" or "physical" point of view.

As has been pointed out, cellulose fibres can undergo chemical reaction without the destruction of the fibre as such, and it therefore appears that reaction should occur within the structural unit of each crystallite without affecting the disposition of the crystallites with respect to one another. Herzog tested this deduction from the X-ray results by determining the size of the colloid particles before and after a chemical change. He was able to show "that the chemical transformation is accomplished within the complex of atoms united in the crystallite without the latter undergoing disintegration to single ($C_6H_{10}O_5$) groups, a conclusion in complete agreement with the results of X-ray analysis." It is of considerable importance to find that the size of the colloid particles (cellulose nitrate) corresponds exactly with the size of the crystallites calculated from the X-ray data.

In a later paper Herzog states that cellulose acetate contains sixteen $C_6H_7(C_2H_3O_2)O_2$ groups in the unit cell, whilst nitrated cellulose contains thirty-two $C_6H_8(NO_3)_2O_2$ groups. The crystals are regarded as under tension along the fibre axis.

The existence of crystallites in natural cellulose does not necessarily indicate that the substance is entirely crystalline. In point of fact, the existence of an isotropic medium in which the tiny crystals are embedded with their principal axis parallel to the fibre axis has been revealed. The X-ray results confirm the assumption of a fairly large proportion of "amorphous cellulose." The possibility of hardening cellulose depends on the existence of this two-phase system. Under stress the crystallites *flow* in the colloidal medium and a more uniform distribution is achieved. The flow is conditioned by the water-content of the cellulose fibre, and hence by the degree of swelling, which is in turn connected

with the breaking stress. In this connection the experiments of Katz and Mark on the swelling of cellulose are of interest. The swelling of chitin cellulose and of fibrin in water causes no change in the crystal lattice. Ramie cellulose, swollen in aqueous solutions (by means of zinc chloride, calcium thiocyanate, potassium iodide, or potassium iodide plus mercuric chloride), likewise shows no change. If, however, a strong solution of caustic alkali or "cuprammonium" solution is used as the swelling agent, an enlargement up to 4 per cent. may be observed. The only artificial silk which fails to show the X-ray diagram of mercerised cellulose is "acetate-silk." The orientation of crystallites in the fibre is regarded as an effect of growth brought about under the influence of tension. In "cuprammonium" silk the orientation becomes increasingly definite as the period over which the fibre is held in tension is prolonged. "Viscose-silk" is made by a rapid process, and, as would be expected, the orientation is less definitely shown.

It is sufficiently obvious that fundamental investigation connecting the strength of fibres with their physical condition will have great industrial significance. The artificial silk industry must be particularly affected, although the secrecy observed with regard to processes prevents an estimate of the actual value of the results being obtained. The X-ray investigations seem to have provided a rational explanation for many observations, and X-ray control of the degree of tension during winding, etc., of artificial fibres may yield important results.

A very recent paper by Hengstenberg (*Ann. Physik*, 1927, [iv], **84,** 245–278) contains some interesting results. Johner and Signer (*Zurich Dissertations*, 1927) have studied the polymerisation of formaldehyde. and many products obtained by them have been subjected to X-ray analysis by the powder method. Highly polymerised polyoxymethylenes of the type

α $HO.CH_2(OCH_2)_x.OCH_2OH$ x=about 60.
β $HSO_3.OCH_2(OCH_2)_x.CH_2O.HSO_3$
γ $CH_3O.CH_2O(OCH_2)_x.CH_2OCH_3$

all show the same X-ray diagram. By heating polyoxymethylenes with acetic anhydride, oxymethylene-diacetates in which x varies from 8–22 can be obtained and separation effected by fractional crystallisation. Using a specially pure 9-CH_2O diacetate the X-ray work leads to the cell dimensions $25{\cdot}2 \times 8{\cdot}30 \times 4{\cdot}47$ Å.$=935$ Å^3, whilst the volume of a single molecule calculated from the density and the molecular weight is 451 Å^3, so that there must be two molecules in the unit cell. When $x=15$ the dimensions $36{\cdot}8 \times 7{\cdot}89 \times 4{\cdot}56$ Å. are found, and there are still two molecules in the cell. For every CH_2O group added the length of the cell increases by about 1·9 Å.

It is therefore clear that in the case of these soluble diacetates the molecule is the "brick" out of which the lattice is constructed. When mixtures of "low" polymerides are examined it is found that molecules of the same length always crystallise together and mixed crystals do not occur. On the other hand, in the diacetates in which x has a high value, and in other highly polymerised products, molecules of different lengths may be attached end to end, so that in this case the lattice cannot be built up on the basis of molecular units. Staudinger has suggested that cellulose is built on the basis of a relatively simple formaldehyde polymerisation product as the unit "brick." Fibre structure would appear to be due to a unidirectional alignment of the *chemical* forces in the lattice. With a more complicated unit "brick" it is reasonable to assume the transmission of chemical affinity in all directions, so that the entire crystallite becomes to all intents a huge single molecule.

X-rays and Rubber.—The fibre structure of cellulose may be regarded as a half-way stage between a single perfect crystal and the random orientation found in a powder. A greater or less tendency towards fibre structure is obtained with cold-working, rolling, or drawing of metals.

Truly amorphous substances are somewhat rare, and the uniform blackening of the photographic plate which is associated with complete absence of regular structure is

only found for mercury, solid alkali metals at fairly high temperatures, and for a few other materials. Liquids, glasses, and colloids all show incipient structure—some degree of regular orientation. Metals give the same diffraction spectra in the colloidal as in the massive state, but the lines become broader with decreasing particle size, and the magnitude of colloid particles in carbon blacks can be calculated from changes in line breadth. Clark and his associates, at the Massachusetts Institute of Technology, have successfully used a pinhole method of X-ray research. A beam of monochromatic X-rays (copper anti-cathode) is defined by two pinholes in lead screens and is then allowed to traverse a specimen placed over the outer pinhole, and the diffracted rays then strike a flat photographic plate.

Ordinary Hevea or vulcanized rubber gives a single broad ring, indicating a near approach to a truly amorphous structure, but conflicting reports have been made as to the structure of raw rubber. Katz examined a number of specimens and observed good crystal interferences except in the cases of dried latex and washed and dried raw Para rubber (although the latter was doubtful), but on heating the specimen any crystal structure permanently disappeared.

Hauser and Mark, and also Clark, failed to satisfy themselves of the existence of crystalline material in raw rubber. Ott, however, examined a specimen of crepe rubber and found interferences, which indicated a cell of side 6·37 Å., a result which led him to conclude that the maximum formula for rubber would be $(C_5H_8)_6$.

Pummerer and Koch have isolated by chemical means a crystalline material of empirical formula C_5H_8 from smoked sheets. Powder photographs indicated a monoclinic lattice with one molecule of formula C_5H_8 per unit cell. Katz failed to make rubber more crystalline by using a freezing process.

Stretching of Rubber.—The peculiar property of rubber which accounts for many of its uses is its elasticity. The X-ray investigation of the stretching process, therefore, gave promise of yielding interesting results. Whenever

rubber is stretched the X-ray diagram undergoes considerable change. Definite interference spots appear with greater and greater definition as the stretching increases, but their positions do not alter. The ordinary pure Hevea rubber shows this effect when the elongation is greater than 75 per cent. From this point onwards the diagram indicates a fibre structure. Vulcanised rubber requires as much as 250 per cent. elongation before a definite crystalline structure makes its appearance, and most synthetic rubbers behave similarly, but provided the stretching has not been excessive the amorphous diagram gradually reappears when the tension is released. When the rubber is cooled after stretching and then released the crystal structure persists for a longer period. Hauser and Mark found that by stretching rubber over a ring, or in two diagonal directions, the diagrams indicated fibreing in two or more directions. They further showed that the effect of stretching is actually to cause the *appearance* of new crystal-like diffracting entities, and the evidence goes to show that the crystals do not exist as such before the stretching process takes place.

The theory advanced by these authors is as follows :

Unstretched rubber is made up of two phases—

(*a*) highly polymerised rubber hydrocarbon (solid phase) swollen by a liquid phase of

(*b*) a less highly polymerised hydrocarbon.

Upon stretching the liquid is squeezed out, and the (*a*) phase is concentrated, and so aligned, that the fibre diagram results.

The lattice dimensions of the rubber crystallites are :

$$8 \times 6{\cdot}5 \times 6{\cdot}5 \times 10^{-8} \text{ cm. (Katz), or}$$
$$7{\cdot}68 \times 8{\cdot}0 \times 8{\cdot}6 \times 10^{-8} \text{ cm. (Hauser and Mark).}$$

The cell is probably orthorhombic, and although it is not clear whether the number of isoprene molecules is 1, 2, 3, 6, or 8 per unit cell, it seems certain that the chemical structure of rubber is in any case much simpler than has hitherto been thought.

The state of knowledge at present reached has been

expressed clearly by Clark (*J. Ind. Eng. Chem.*, 1926, Nov. p. 1135): "The facts brought out by the X-ray examination explain those properties which so peculiarly characterise rubber. During stretching, for the first 75 per cent. in pure rubber a gel substance characterised by small fluidity and large elasticity predominates. From this on threads of meta crystals of a strongly cohesive and much less ductile substance account for the much smaller elongation for a given force before breaking. The effect discovered by Joule in 1857, that rubber heats upon being stretched while other substances cool, is explained by the heat of crystallisation.

"Upon the basis of the X-ray structures, the material might be expected to cool in the first stages of stretching. Joule found that this was indeed true for rubber. The increase in intensity of the X-ray diffraction interferences with increasing tension on the rubber is, however, difficult to relate to the Joule effect as it is now known, because the curve for this effect rises to a marked maximum and falls off. Further precision experiments are urgently needed." Clark and Brugmann have also studied balata and gutta-percha (*loc. cit.*). It is stated that as yet unpublished experiments on gelatin, collagen, glue, shellac, etc., have given interesting results.

Irrespective of the survival-value of the theories now in vogue, it must be conceded that the X-ray studies of rubber and similar "colloids" cannot fail to clarify our ideas in a very valuable way as better experimental data and reliable interpretations accumulate.

X-rays and Medicine.—The application of X-ray photography to diagnosis depends on the relative opacity of bone and flesh to the passage of the rays. From the strictly chemical point of view X-ray shadowgraphs are of little interest. The use of bismuth salts as an opaque lining for showing up the alimentary canal, of red lead for rubbing into finger tips for recording the design of finger prints are, however, interesting side lines.

X-ray therapy is a promising field for chemical research,

although little is known concerning the reactions involved. Lupus, rodent, and malignant disease have responded to treatment, but X-ray therapy remains largely a gamble except in some diseases like ringworm, eczema, and sycosis. X-rays have little or no bactericidal action. One of the great difficulties in radio-therapy is the control of dosage. The following methods have been proposed :

(1) Discoloration of alkali salts (Holzknecht, 1902).
(2) Liberation of iodine from 2 per cent. solution of iodide in chloroform (Freund, 1904).
(3) The darkening of photographic printing paper (Kienbock).
(4) Precipitation of calomel from solutions containing mercuric chloride and ammonium oxalate (Schwarz, 1907).
(5) The change of colour of pastilles composed of barium platinocyanide $BaPt(CN)_3.4H_2O$ (Sabourand-Novie and Bordier).
(6) Lowering of electrical resistance of selenium.

None of these methods is really satisfactory, and the results are only capable of giving a rough guide to dosage.

In his fascinating book, *Practical Applications of X-Rays*, G. W. C. Kaye records the practical depths which can be penetrated in various materials for the examination of flaws, etc.

4–5 mm.	lead,
12 mm.	tin,
5 cm.	brass,
7–5 cm.	steel (carbon) or iron,
10–15 cm.	aluminium or its alloys,
30–40 cm.	wood.

Kaye points out that X-ray inspection has the advantage of not injuring the material in any way, furthermore, it provides in many cases the only means independent of human judgment of detecting concealed defects in an article, or of scrutinising in a structure the accuracy of assembly of component parts which are concealed from view. Hidden flaws in a metal and blisters and blow holes in welds may be

detected, and defective filling of explosive shells may be demonstrated. Internal details of captured enemy explosives may be disclosed without danger. Knox and Kaye during the war applied X-rays to the detection of minute flaws in wood and in alloys intended for aircraft. "In the manufacture of golf balls fine rubber tape is wound on a spherical core either of soft rubber or liquid. If care is not taken the core is distorted, becoming either roughly ellipsoidal or even dumb-bell shaped. The resulting ball is defective from the point of view of accurate flight, but such balls can readily be sorted out by the help of the X-rays. The balls are allowed to roll slowly between the tube and a fluorescent screen and examined as they pass. The method is now in extensive use, no other being readily available" (Kaye, *Practical Applications of X-rays*).

"Perhaps the most interesting application of X-ray shadowgraphs to the chemist is in the investigation of 'Old Masters.' The early painters had very few pigments, and these were mostly inorganic. X-rays have proved of great assistance in determining the genuineness of a given painting.

"In any picture we have to consider three media:

"(1) The surface which is painted on—usually canvas or wood, though paper, porcelain, or other materials may be used.

"(2) The painting or sizing, nowadays almost always white-lead, though formerly carbonate of lime and glue were employed.

"(3) The actual pigments.

"Both wood and canvas are very transparent to the X-rays, though different kinds of canvas vary a good deal. The white-lead primer is much more opaque than carbonate of lime, and the former, moreover, penetrates much farther into the interstices of the canvas. This in itself is sufficient to show a marked difference under the X-rays between modern and older pictures.

"As to pigments, they vary greatly in X-ray opacity, from the opaque salts of lead, zinc, and mercury, to the

transparent aniline derivatives and bitumen. Both modern and ancient whites are usually opaque, most of the blacks (new or old) are transparent, and modern reds are more transparent than the old reds. In general, as already remarked, most of the earlier pigments are mineral in origin and opaque, while most of the modern pigments are coal-tar in origin and transparent.

" In a modern picture the sizing is very commonly more opaque than the pigments, and X-ray examination is, for that reason, usually inconclusive. In a radiograph of a modern painting little can be seen but the canvas and a trace of the white pigment. But fortunately in the pictures of the Old Masters the reverse conditions hold, and thus it is that with a little experience, and if the relative opacity of the various pigments is such as to yield good contrast, the X-rays can be employed most usefully as a means of identifying a modern fake, or detecting alterations to an old picture. It is a practical certainty that, however skilfully the process has been carried out, the several materials used—whether canvas, priming, or pigment—will differ from those in the original painting, and will, in consequence, be differentiated in the radiograph " (Kaye).

Kaye gives instances in which paintings were " restored " to please the owner for the time being by painting fresh figures over the originals or else by removing so-called defects.

It has been possible not only to detect this kind of thing, but to use the X-ray photographs as guides to the restoration of the original painting.

X-rays and New Elements.—One of the first fruits of the well-known X-ray work of Moseley in establishing the simple relation between characteristic X-ray wave-lengths and atomic number was the elucidation of the problem of the positions of iron, nickel, and cobalt in the periodic table. Moseley's investigations also defined quite clearly the number of elements remaining undiscovered. The work was brilliantly continued by Siegbahn and his associates. Hadding was able to demonstrate the im-

portance of X-ray spectra in the field of the rare earths, and Goldschmidt and Thomassen gave a rough estimate of the proportions of the rare-earth elements present in practically every important ore. Coster and Hevesy's work on hafnium owed its success largely to the X-ray weapon. In order to detect and estimate hafnium, a known amount of tantalum oxide was ground up with the sample of ore and the relative intensities of the corresponding tantalum and hafnium lines were determined. After this method had proved successful in controlling operations which ended with the isolation of pure hafnia another method was substituted. In order to estimate the hafnium content of a sample, the material (in the form of oxide) was mixed with a known amount of lutecium oxide. By comparing the intensities of the $Lu\beta_2$ and $Hf\beta$ lines (*i.e.* closely related lines for the neighbouring elements of atomic numbers 71 and 72) it was possible to determine the hafnium content. The procedure had, of course, been previously " calibrated " by the use of pure lutecia and pure hafnia under standard conditions.

Hevesy points out that the introduction of X-ray spectroscopy constitutes a fundamental step forward in analytical chemistry. His reasons may be summarised as follows :

(1) As X-ray spectra are connected with the temporary removal of electrons from inner electronic groups, whilst optical spectra are connected with the removal of outer electrons, X-ray spectra are necessarily less complex than optical spectra.

(2) In contradistinction to optical spectra, X-ray spectra are little affected by the state of combination of the elements concerned.

(3) The position of the lines in X-ray spectra may be calculated in advance, a fact of great importance in searching for missing elements.

(4) The exitation of the lines in X-ray spectra is easily regulated.

(5) Any element from sodium to uranium can be identified by its K-lines and from copper to uranium by its L-lines.

An instructive illustration of the application of X-ray methods is to be found in Hevesy's treatment of the problem of the detection of tantalum. The mineral under investigation is powdered and placed on the anti-cathode of the X-ray tube. The strong L-line is first sought, using a vacuum X-ray spectrograph and about 10,000 to 18,000 volts on the tube. If this line appears at 1,518 XU (1·518 Å.U.), this will only constitute an unequivocal proof of the presence of tantalum if the position of the line is measured to an X-unit. Unless the degree of accuracy is very high X-ray spectroscopy has always to contend with the difficulty of coincidences in this case of TaL with DyL_5. Now, if dysprosium is present the DyL (strong line) must occur, and the absence of this line rules out the coincidence. On the other hand, coincidences may occur, and perhaps the safest way is to excite the B_1B_{22} lines, etc., of the tantalum spectrum, again eliminating possible coincidences. Besides the emission lines the absorption edges have been used to identify elements.

Sufficient has been said to indicate the general line of procedure. It must be clear that satisfactory evidence for a new element cannot rest on mere observation of weak lines, the observations must be so controlled as to eliminate coincidences.

Hevesy states, " The X-ray method was not only found to be a unique analytical weapon in the discovery of the element 72, but also in the process of isolating hafnium when the method was employed to check the result of every step in the prolonged process of separation."

The remaining unknown elements are 43, 61, 75, 85, and 87. Noddack, Tacke and Berg claimed to have secured X-rays lines of elements 43 and 75, and have used the names masurium and rhenium respectively for the metals. Heyrowsky and Dolejsek also record lines of element 75 in preparations extracted from " pure " manganese com-

pounds. The results on 43 and 75 lack corroboration as yet.

As regards element 61, a rare earth, Harris, Yntema, and Hopkins obtained indications by means of absorpton band spectra of the presence of a new element in their preparations. Faint X-ray lines were recorded. In the case of illinium, as this element is called, the X-ray work has been corroborated by German workers. The outlook as far as X-ray work is concerned is not very bright in connection with the elements 85 and 87.

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APPENDIX I

Electrostatic Precipitation

It might be thought that the electrical deposition of dust and smoke hardly comes within the scope of the present work. Nevertheless, the gap which separates the photo-electric effect from the action of the silent electric discharge and the brush discharge is not a large one, and some consideration of electrostatic precipitation is not out of place.

Sir Oliver Lodge, as far back as 1886 (*Jour. Soc. Chem. Ind.*, Nov. 29), published an important paper under the title "The Electrical Deposition of Dust and Smoke, with Special Reference to the Collection of Metallic Fume, and to a possible Purification of the Atmosphere." Tyndall discovered that a dark or dust-free space was formed over a hot body placed in strongly illuminated dusty air. Lodge guessed that air in streaming over the surface of the hot solid body might become electrified and that dust might thereby be expelled. In order to test this hypothesis he purposely electrified a rod both positively and negatively, but found that the effects with one or two hundred volts were barely noticeable. As soon, however, as potentials of a few thousand volts were applied and brush discharges began to occur, a very remarkable effect was observed, and the whole of the dust or smoke in the experimental box was rapidly precipitated. It was found that the brush discharge or any means by which the air itself could be electrified resulted in the effective elimination of suspended particles of dust. "The electrified or polarised particles attract each other and are attracted by the opposite poles just as iron filings are influenced by a magnet."

In many industries suspensions of dust or fumes occur which

are very objectionable either because of pollution of the atmosphere or because of danger in or out of the factory, or else because the occurrence of volatile " fume " means the loss of a valuable product. In coal-mines and in flour-mills the dust hazard is serious, because of the risk of explosions, whilst the liberation of lead-copper or arsenic-bearing fumes is undesirable, both on account of financial loss and of the poisonous nature of the substances set free. Lodge's suggestion was " to line a certain portion of the interior (of a chimney or flue) with spikes and then to hang in the middle of it wire netting, well insulated and studded all over with ragged edges and points. This should be placed lengthways in the flue." If a large chamber were available for dealing with the fumes, it was suggested that a number of long prickly nets should be placed parallel to one another and charged alternately positive and negative. Lodge's concluding sentence is worth quoting, " I do not regard this as a good method for dealing with smoky chimneys. The right way to deal with them is to abolish them, *i.e.* to make combustion so perfect that no unburnt matter escapes. The experiments illustrate, however, that smokes can be caught and deposited on the wing."

Lodge's laboratory experiments had been so brilliantly successful with the following smokes : tobacco, burning brown paper, camphor, turpentine, magnesium oxide, ammonium chloride, ammonium sulphite, phosphorus pentoxide, steam, lead fume, zinc fume, etc., that it was thought worth while to try out large-scale experiments.

At Bagillt in North Wales, Messrs. Walker, Park and Co. were troubled with lead fume, although a large flue two miles long was coiled up the side of a hill between the furnace and the chimney. In spite of the enormous length of flue a white cloud of lead-bearing fume escaped from the chimney. Electrodes were arranged in the flue and were charged by means of two Wimshurst machines with glass plates 5 feet in diameter driven by a single horse-power engine. The experiment was not a great success, owing, there can be no doubt, to the fact that the current available was far too small.

Lodge's pioneer work was not followed up very effectively until 1905, when F. G. Cottrell began to study the effect of high-

tension current on the precipitation of sulphuric acid mist in the contact process. By this time the generation of high tension was a much easier proposition than in 1886. Direct current is troublesome to step up to give high tension, owing to the difficulty of maintaining good insulation, but alternating current of low voltage can easily be stepped up and used as high tension alternating current or rectified and used as intermittent direct current. Cottrell found that as a rule alternating current produces agglomeration with the formation of large flakes, which settle fairly rapidly in still gas. For rapidly moving gases, such as the fumes from smelting furnaces, the direct current is to be preferred, as the particles of suspended matter can then be driven to a suitably arranged collecting electrode. The exact arrangements used in the various Cottrell processes would take too long to give in detail. The main facts are that potentials of 20,000–100,000 volts are used between electrodes of wire net or plates, according to the special circumstances of each plant.

The Cottrell process has been applied to the precipitation of sulphuric acid mist from a contact process in Mannheim. The voltage used is 6,600, and the wattage is 1·6 Kw.

The following details apply to a large smelting plant:

Flue 18 by 20 feet; linear velocity of gas 10 to 20 feet per sec.; voltage 25,000 to 30,000 120 Kw.; temperature 100 to 150° C.; nine precipitators; efficiency 80 to 90 per cent.

The process has been applied both in England and in America to the treatment of sulphuric acid mist, using electrodes of lead. One plant is quoted by Gibbs as yielding 25 tons of 40° Baumé acid from gas passing through at enormous velocity.

Blast furnace gas can readily be cleaned by means of the process. In other cases it is feasible to precipitate the suspended matter in fractions, so that a valuable degree of separation of the fume constituents can be achieved. Chlorine-bearing gas from bleach chambers can be treated with lime powder and the resulting bleaching powder precipitated electrostatically. When phosphatic rock is heated with coke and silica in the electric furnace phosphorus pentoxide is liberated and may be precipitated electrostatically as acid. It is stated that nitric acid clouds

formed in the Haber process, lamp black under certain conditions, and other suspensions have also been successfully treated by the Cottrell process.

The original memoirs should be consulted for further details.

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APPENDIX II

ABSORPTION spectra enter so much into photochemistry that a few words on technique may not be out of place, although Baly's *Spectroscopy* is indispensable in this field. For a general survey of the spectral absorption of a substance a Hilger quartz spectrograph E3, fitted with a long focus rotating disc sector photometer and using an arc between iron and nickel poles, is, in the author's opinion, by far the best method. For work involving special accuracy, a tungsten spark under water using a Tesla discharge provides the best spectrum, as it is quite continuous from the red to 210$\mu\mu$. With this light source a short focus sector photometer should be used in order to shorten the exposure. There is, in the author's opinion, little to choose between the Judd Lewis photometer and the ordinary sector photometer, but for work involving the highest accuracy the advantage is with the former. For the investigation of fine structure in an absorption band, the best method is to use the continuous spectrum and to measure the plate by means of registering microphotometer. For the investigation of absorption spectra in the visible the small dispersion of the ordinary quartz spectrograph precludes the highest accuracy, and it is necessary to turn to a larger spectograph of the Littrow type if a photographic record is desired, but for most substances the least troublesome method is to use a visual apparatus of the Nutting or Keuffel Esser type. The wedge spectrograph has a distinct if restricted field of utility for rapid qualitative work in the visible region.

Much useful information is to be found in a booklet published by Adam Hilger, Ltd., entitled *Optical Methods in Control and Research Laboratories.* 1925. *2s. 6d.*

APPENDIX III

Constants concerning Radiation and Chemistry

R	Gas constant for one gram molecule	$8{\cdot}315 \times 10^{7}$ ergs/gm. deg.
N	Avogadro's Constant	$6{\cdot}062 \times 10^{23}$
h	Planck's Constant	$6{\cdot}558 \times 10^{-27}$ erg. sec.
c	Velocity of light	$2{\cdot}9986 \times 10^{10}$ cm. sec.$^{-1}$.
e	Charge on the electron	$1{\cdot}592 \times 10^{-20}$ E.M.U. $4{\cdot}774 \times 10^{-10}$ E.S.U.
m	Mass of the electron	$9{\cdot}04 \times 10^{-28}$ gm.
M	Mass of the hydrogen atom	$1{\cdot}649 \times 10^{-24}$ gm.

Chance, 41, 43
Chapman, 75, 81
Chardonnet, 187
Chattaway, 103
Christiansen, 14
Ciamician, 103
Clark, 59, 75, 134, 194, 256, 258
Coblentz, 68, 133
Coehn, 79, 81
Coolidge, 228, 229, 230
Cooper-Hewitt, 25
Coster, 262
Cottrell, 268
Crichton, 224
Crookes, 36
Cruickshank, 203, 205
Cunliffe, 106
Curie, 180
Curtis, 72, 121
Custis, 124

Daguerre, 137
Daland, 195
Daniels, 6
Davies, 82, 85, 88
Debierne, 182
Debye, 130, 236
De Fazi, 103
Dehlinger, 265
Devers, 38
Dewey, 62, 92
Dickinson, 70
Dolejsek, 263
Dorée, 96
Downes, 70, 93, 195
Draper, 3, 50, 51
Driffield, 147, 151
Drummond, 208, 209
Dubois, 191
Duclaux, 144
Dufraisse, 92
Dufton, 43
Dyer, 96

Ebert, 248
Eder, 52
Egbert, 270
Eggert, 50, 121
Eidinow, 52, 53
Einstein, 4, 8, 10, 74, 104, 136, 159
Elder, 124
Eldridge-Green, 188
Ellis, 109, 110, 122, 197, 200, 206
Elster, 159
Elvejem, 224
Emschwiller, 109
Esser, 43
Essex, 117
Euler, 98

Fabry, 74
Fajans, 131, 132
Farber, 93
Faucon, 56, 119
Feder, 86
Federlin, 93
Fehling, 100
Feick, 129
Fenton, 78
Ferguson, 206
Ferrier, 92
Finsen, 202
Fischer, 75
Flynn, 105
Foex, 244
Forest de, 162
Franck, 12, 13
Frankenberger, 131
Frankenheim, 231
Fraünhofer, 15
Frese, 160
Freund, 259
Friedrich, 232
Fulweiler, 23
Furstenhaus, 53

Gamble, 42
Gamgee, 206
Gardner, 43
Garrison, 164
Gaudechon, 80, 92, 95, 96
Gaudin 38
Gebhard, 105
Geiger, 121, 122, 158
Geissler, 21, 75
Geitel, 159
Genthe, 101
Gibbs, 121, 122, 269
Gibson, 25
Gillam, 54, 56, 57, 62, 65
Glew, 178
Glitscher, 198
Glocker, 265
Glysyn Corpn., 124
Goldschmidt, 262
Goldstein, 74, 75
Gook, 121
Gordon, 105
Graul, 123
Graves, 75
Gray, 110
Griess, 58
Griffith, 76, 161, 162
Grossman, 95
Grotthus, 3, 11, 50, 51
Grüss, 9, 50

Haber, 270
Hadding, 261

Hagenbach, 198
Halban, 162
Hall, 206
Hanschke, 123
Harris, 264
Harrison, 105
Hart, 224, 225
Hartley, 103
Hartung, 129
Harvey, 190, 191, 192
Hasselbach, 198
Hauser, 256, 257
Hauy, 231
Hecht, 188
Hedvall, 47
Heilbron, 80, 85, 101, 211, 213, 215, 217, 218
Heimrod, 270
Heindlhofer, 246
Helbronner, 106, 200, 201
Helmholtz, 154
Henderson, 224
Hengstenberg, 254
Henri, 5, 11, 53, 71, 95, 96, 97, 98, 100, 107, 150, 197, 200, 201
Herchefinkel, 80
Hertel, 119, 120
Herzog, 251, 252, 253
Hess, 96, 99, 207, 210
Hevesy, 262, 263
Heyrowsky, 263
Hibben, 7
Higgins, 226
Hill, 44, 52, 53, 206, 207
Hinshelwood, 7
Hobler, 157
Holzknecht, 259
Hood, 87
Hooker, 188
Hopkins, 264
Howe, 25
Howell, 44
Hudson, 101
Huldschinsky, 207
Hull, 237, 240
Hume, 207
Hurter, 109, 147, 151
Hislop, 157
Hughes, 195, 225
Humphris, 206
Hyslop, 250

Ilosvay, 58
Ives, 193

Jack, 162
Jakowsky, 107
Jancke, 264
Jeantet, 144
Jendrassik, 217
Jette, 248
Job, 109
Johner, 254
Johnson, 82, 85
Jorrissen, 101
Joule, 258
Jovitschitsch, 79

Kailan, 97, 103
Kabler, 68
Kamm, 198, 211, 213, 215, 217, 218
Kassel, 75
Katz, 254, 256, 257
Kaufmann, 96
Kaupp, 265
Kautsky, 193
Kaye, 259, 260, 261
Keller, 52
Kelley, 156
Keményffi, 217
Kempfe, 108
Kernbaum, 70, 79
Kettnow, 112
Keyes, 116
Keuffel, 43
Kienboch, 259
Kindall, 186
King, 30, 55, 206
Klatt, 159, 168, 172, 175
Klatte, 92, 94
Klein, 195
Knapp, 62, 63, 64
Knipping, 232
Knox, 260
Koch, 129, 130, 256
Kolzareff, 158
Konig, 140
Kordatzki, 109
Kornfeld, 50, 72
Kramers, 14
Kremann, 77
Kreuler, 79
Kriess, 129
Kromayer, 30
Kuch, 31
Kuhl, 94
Kummerer, 103
Kunz, 75

Lacy, 116
Lamb, 270
Lambert, 3, 50
Langley, 15
Lasareff, 11
Läue, 229, 232, 246
Laurens, 188
LeBlanc, 123
Ledanburg, 74
Leemans, 183

Lehmann, 74
Leiser, 115
Lenard, 74, 159, 168, 172, 175
Levy, 174
Lewis, G. N., 6
Lewis, Judd, 271
Lewis, W. C. McC., 5
Lilienfeld, 230
Löb, 79
Lodge, 267, 268
Long, 68
Losanitsch, 79
Loveland, 136
Lovibond, 49
Lowry, 31, 49
Luckiesch, 35
Lumiere, 142, 143, 155
Lunt, 79
Luppo-Cramer, 138, 142
Luther, 93

Maas, 108
Macaulay, 103
Macbeth, 24
McHatton, 49
McHugh, 103
McKenzie, 30, 55, 206
McKeown, 76
MacLean, 222
Malkin, 250
Mallet, 150
Marc, 158
Marcusson, 93
Mark, 254, 256, 257
Martin, 42, 187
Massol, 56, 100, 119
Mathews, 62, 72, 103, 124
Matignon, 183
Maxwell, 154
Mayer, 6
Meyer, 52
Michaud, 113
Miethe, 112
Miller, 38
Millikan, 159, 160
Millington, 246
Mills, 140, 141
Minchin, 163
Molisch, 88
Montgomery, 118
Moore, 21, 24, 85
Morgan, 196, 198
Morrison, 193
Morton, 54, 57, 62, 65, 82, 150, 198, 211, 213, 215, 217, 218
Moseley, 238, 261
Moss, 62
Mott, 24, 105, 122
Moureu, 92

Nelson, 68, 208
Nernst, 13
Nishizawa, 108
Noddack, 9, 50, 263
Nogier, 201
Noyes, 75
Nutting, 45

Ohlsen, 98
Okimaka, 118
Orr, 224
Orton, 103
Osmond, 242
Ostromuislenski, 93
Ostwald, 78
Ott, 264
Otto, 201
Owen, 179, 248

Pacini, 206
Padget, 123
Paget, 156
Pappenheimer, 207
Pasteur, 83
Pauthenier, 96
Payne, 118, 225
Perman, 75
Perrin, 5
Pfeifer, 118
Pfund, 109
Phragmen, 231, 243, 244, 248, 249
Pierce, 105
Pincussen, 194
Pintsch, 19
Piper, 251
Planch, 1
Plank, 206
Plotnikow, 10, 13, 93, 150
Pohl, 212
Polanyi, 264
Pope, 157
Popp, 227
Porter, 81, 86, 96
Potapenko, 113
Potter, 75
Preston, 248
Price, 157
Priestley, 80
Pummerer, 256

Ramsbottom, 81
Ramsperger, 7, 81, 86, 96
Ranc, 95, 96, 97
Ransford, 123
Rawling, 136
Rebmann, 81
Regener, 74

Rice, 7, 14, 103
Recklinghausen, v., 197, 200, 201
Rideal, 75
Riding, 81, 150
Ries, 158
Ringer, 101
Rinmann, 45
Robert, 101, 103
Robertson, 150
Robinson, 62
Roches, 107
Rodebush, 118
Rollier, 202, 206
Röntgen, 231
Rosanoff, 71
Rosenhain, 248
Rosenheim, 212, 216, 217
Roy, 14
Rubner, 88
Rudberg, 96
Rupert, 106
Russ, 196
Russell, 206

Sabourand-Novie, 259
Sachs, 250
Sakai, 118
Sand, 31
Schall, 206
Schaum, 129
Scherrer, 130, 236
Scheurer, 105, 130
Schleede, 109
Schlutz, 210, 211, 223
Schmiderschitsch, 77
Schmieder, 176
Schmitt, 97
Schmitz, 124
Schoenfliess, 231
Schopper, 107
Schumann, 144
Schwarz, 259
Schwarzschild, 149, 150
Scott, 103
Selden, 124
Seyewetz, 142, 143
Shannassy, 85
Sheard, 226
Shearer, 231, 250
Sheppard, 135, 136, 146
Sheringham, 41
Shutt, 77
Siegbahn, 231, 236, 243, 261
Sieper, 81
Signer, 254
Silber, 103
Smith, 6, 7, 117, 152, 200, 207
Snelling, 115, 116
Sohncke, 231
Spallanzani, 191
Spoehr, 81
Stark, 8, 31, 161
Staudinger, 255
Steel, 96
Steenbock, 208, 224
Steiner, 132
Steinberger, 103
Stengel, 112
Stern, 12, 101
Steven, 87
Stobbe, 93, 97, 103
Stoermer, 101, 103
Stokes, 138, 144, 167
Stoklasa, 80
Stoll, 77
Suida, 101
Szarvasy, 118
Szilard, 161

Tacke, 263
Taylor, 14, 72, 161
Thenard, 45
Thiele, 70, 79
Thomas, 222
Thomassen, 262
Thompson, 7, 246
Thum, 270
Tian, 71
Toepfer, 93
Tollett, 92, 94
Tolman, 14
Tompkins, 115
Toy, 133
Trautz, 5
Trendelenburg, 189
Tristan, 113
Trivelli, 136
Troup, 206
Tucker, 165
Tyndall, 267

Unger, 207
Urbain, 173
Usher, 80

Van't Hoff, 11
Villars, 57, 58
Vogel, 138
Vogler, 129
Volmar, 121
Volmer, 12

Walsh, 15, 19, 21, 4
Warburg, 8, 9, 50,
Ward, 195
Wastell, 157
Watkins, 150

Watt, 203
Webster, 52, 53, 85, 207, 212, 216, 217
Weigert, 9, 75, 76, 93, 103
Weimarnn, 145
Weinstock, 207, 210
Weiss, 244, 265
Wells, 110, 197, 200, 206
Wenther, 10
Westgren, 231, 243, 244, 246, 248, 249
Whiston, 124
Wildermann, 164
Williamson, 103
Willoughby-Smith, 158
Willstatter, 77
Wilson, 103
Windaus, 212
Wood, 101, 113
Wright, 110
Wulf, 22
Wurmser, 5, 71, 95, 96
Wyckoff, 48, 236
Wynne, 150

Yntema, 264

Zdobnicky, 80
Zenghelis, 82
Ziegler, 210, 211
Ziffer, 115
Zsigmondy, 36

SUBJECT INDEX

Absorption, 3, 4
Acetaldehyde, 7, 95, 98
Acetamide, 101
Acetanilide, 101
Acetate silk, 254
Acetic acid, 95, 120
Acetoacetic ester, 95
Acetone, 9, 95, 97
Acetone-methylene blue, 54
Acetyl acetone, 95
Acetylchloraminobenzene, 103
Acetyl chloride, 120
Acetylene, 92
Acrolein, 92
β-Acrose, 97
Actinometry, 50, 66, 161
Actinotherapy, 202
Activation, 7, 12
Ageing of dyestuffs, 104
— of paints, 106
— of quartz, 28
— of rubber, 106
Albumen, 193
Aldoximes, 103
Alfalfa seed oil, 219
Alkaloids, 101
Alkyl halides, 97
Allotropy, 241
Alloys, 247, 249
Allyl *iso*selenocyanate, 136
— *iso*thiocyanate, 136
— thiocarbamide, 135
— thiocarbimide, 135
Aluminium bronzes, 247
Amino acids, 197
Animal nutrition, 224
Anomalops, 188
Anthracene, 93
Anti-rachitic materials, 208
Aposafranine, 143
Arsenite, 134
Atomic number, 238
Austenite, 245
Autochrome, 155
Avogadro number, 240

Babassu oil, 219
Bacteria, phosphorescence of, 188
Bactericidal action, 57, 196
Balata, 258
Barium platinocyanide, 174
Beer's law, 3, 162
Benzal chloride, 122
Benzaldehyde, 101
Benzanilide, 101
Benzene, 117
Benzotrichloride, 122
Benzoyl acetyl peroxide, 101
— acrylic ester, 103
— phenylethylene oxide, 103
Benzyl chloride, 121
— violet 5BN, 42
Bichromated colloids, 152
Bismuth trisulphide, 158
Blood, 193
Blue prints, 156
Brasses, 249
Brazil-nut oil, 219
Brightness, 22
Bromide body, 131
— paper, 137, 146, 147
Bromination, 123
Burnt umber, 39
Butyric acid, 120

Cadmium cell, 161
— lamp, 31
Calcite, 240
Calcium cycle, 225
— glycollate, 83
— lactate, 95, 223
— metabolism, 223
— phosphate, 224
— tungstate, 145
Calorex glass, 64
Caramel, 96
Carbocyanines, 139
Carbohydrates, 84, 85
Carbon arcs, 24, 162, 204
— dioxide, 77
— disulphide, 22, 96, 119

Carbon monoxide, 80, 82
— tetrachloride, 9, 55, 115, 119
Carnotite, 181
Carotin, 77
Catalysts, 118
Cataract, 194, 223
Cellulose, 96, 105, 255
— acetate, 252
—, amorphous, 253
— nitrate, 252
—, X-rays and, 251
Cementite, 245, 246
Cerulean blue, 39
Chain mechanisms, 13
Chance's glass, 43
Characteristic, 146
Chemiluminescence, 193
Chinese white, 39
Chlor-benzyl chloride, 122
Chlorination, 113
Chlorine monoxide, 7, 9
Chloroform, 115, 119
Chlorophyll, 77
Chlorplatinic acids, 10
Chlortoluene, 121
Cholesterol, 208, 210
Chromates, 152
Cinnamic acid, 103
Cinnamylidenemalonic acid, 103
Clam, 188
Clay, 250
Coal gas, 19
Cobalt carbonate, 87
— colours, 45 *et seq.*
— glass, 113
Coconut oil, 219
Cod-liver oil, 207, 208, 219
Cohenite, 246
Cold light, 188
— working of metals, 250
Collisions, 7, 12, 76
Collodion, 146
Colloidal metals, 256
Collotype, 153
Coloured surfaces, 89
Colour matching, 49
— photography, 154
— printing, 154
— specification, 43
Conjunctivitis, 187
Continuous spectrum, 23
Coolidge tube, 230
Copper-aluminium system, 247
Corona discharge, 79
Cotton-seed oil, 219, 220
Cottrell process, 268
Coumaric acids, 103
Crookes glass, 36, 37
Crotonic acid, 103
Crystal lattices, 232, 239
Cubic lattices, 239
Cuprammonium silk, 254
Cyanine, 141
Cyanogen, 92
Cyclohexane, 9
Cypridina, 188

Daguerrotypes, 137
Daylight, 150
— glass, 43
Deficiency diseases, 206
Density, 147
Deterioration of lamps, 68
Development, 148
Dextrin, 96
Diacetyl, 96
Dianthracene, 93
Diastase, 194
Dicyanine, 141
Dielectric constant, 129
Diiodoethylene, 96
Diphenylene ethylene, 92
Diphosgene, 121
Dosage, ultra-violet, 205
—, X-ray, 259
Drying oils, 93
Duralumin, 250
Dyestuffs, 104

Eczema, 259
Egg production, 225
Electromagnetic waves, 1
Electrostatic precipitation, 267
Elements, new, 261
Emulsions, 146
Enzymes, 193
Eosin, 160
Epidermis, transmission of, 198
Equivalence, law of photochemical, 4, 104, 136
Ergosterol, 212, 218, 226
Ergot, 217
Erythema, 205
Erythronic acid, 85
Erythrosin, 139
Ethane chlorides, 115
Ethyl acetoacetate, 95
— alcohol, 95
— cyanine, 139
— ether, 120
— malonate, 120
— mesityloxidoxalate, 93
— red, 139
Ethylene, 92
Eugenol, 101
Excited molecules, 11, 13, 70
Exposure meters, 150
Eye, 186

Fats, sterilisation of, 200
Fatty acids, structure of, 250
Ferrite, 245
Fibres, 254
Filaments, 20
Filters, 110
Firefly, 188
Fish, luminous, 188
Flame arc, 24
Fluorescein, 161
Fluorescence, 11, 12, 114
Fluorite, 36, 113
Food (irradiation of), 226
Formaldehyde, 78, 80, 81, 254
Formamide, 95
Formhydroxamic acid, 101
Formic acid, 80
— — peroxide, 78
Fructose, 96
Fugitive pigments, 41
Fumaric acid, 103
Fused quartz, 175

Gas mantles, 19
— Regulation Act, 20
— tubes, 239
Gases, photochemical reactions of, 74 *et seq.*
Gaslight paper, 137, 146, 149
Gamma, 147
Gelatin, 135, 146
German Fastness Commission, 106
Germination of seeds, 226
Glass, Chance's, 43
— coloured, 35
— discoloration, 35
Globulin, 78
Glow-worm, 193
Glucose, 96
Glyceric aldehyde, 95
Glycerol, 85, 95, 97
Glycerose, 95
Glycine, 103
Glycol, 85
Glycollic acid, 85
— aldehyde, 79
Grain size, 146
Graphite, 245
Grotthus-Draper law, 3, 52, 209
Ground-nut oil, 219, 222, 223
Gutta-percha, 258

Hafnium, 262
Halogenation, 113
Hexose, 85
Homocol, 140
Hydrogen, 13
— atoms, 13, 70
— bromide, 9
Hydrogen chloride, 13
— iodide, 9
— peroxide, 10, 70, 79
Hydroxide body, 132

Illinium, 264
Illipé-nut oil, 219
Image, latent, 127
—, visible, 130
Indene, 93
Inhibition, 72
Ink testing, 106
Intaglio printing, 151
Inversion of sugar, 96
Invisible image, 127
Iron, 241
Iron-carbon system, 244
Irradiation of animals, 225
— of cholesterol, 210
— of egosterol, 212
Isomeric change, 103
*Iso*butyric acid, 120
Isocol, 140
Isocrotonic acid, 103
Isocyanine, 141
Isoeugenol, 101

Joule effect, 258

Kapok-seed oil, 218, 220
Kryptocyanine, 141

Lactation, 224
Lactic acid, 95
Lambert's law, 3
Latent image, 127
Läue photographs, 232
Leg weakness, 224
Light therapy, 202
Linseed oil, 219
Lithography, 151
Lithopone, 107
Luciferase, 191
Luciferin, 191
Luminescence, 158, 166
—, animal, 188
Luminogen, 160
Luminous paint, 179
Lupus, 202, 259
Lutecium, 262

Magnetic iron, 242
Maize oil, 219
Malachite green, 161
Maleic acid, 103
Maltose, 96
Martensite, 245
Masurium, 263
Mercerisation, 252

Mercury lamp, 105, 204
— —, K.B.B., 26, 204
— —, Kromayer, 30
— —, Uviarc, 30
— —, Vacuum (Hewittic), 28
Metal arcs, 24
— sparks, 23
Methane, chlorination of, 114
Methylamine, 101
Methyl bromide, 235
— chloride, 115
— formate, 121
— iodide, 234
— sulphate, 121
Methylene, blue, 54
— chloride, 115
Milk, 199, 226
Molybdenite, 158
Molecular phases, 11
Monobromacetic acid, 96
Monochloracetic acid, 96
Monochromatism, 110
Mullite, 250

Natural gas, 114
Nickel carbonate, 86
Nitrates, 57
Nitrogen compounds, photosynthesis of, 101
Nitrogen pentoxide, 5
Nitrous oxide, 7
o-Nitrobenzaldehyde, 9, 103
o-Nitrosobenzoic acid, 9, 103
Nujol, 144
Nutting photometer, 46, 271

Oils, action of light on, 109, 219
Old masters, 260
Opacity, 147
Orthochromatism, 138
Orthochrome T, 139
Ostelin, 219
Oxalic acid, 62, 95
Oximes, 103
Oxygen, 74
Oxyluciferin, 191
Ozone, 9, 71, 74, 75

Paget process, 156
Palm oil, 219
Palm-kernel oil, 219
Paper, 110
Panchromatism, 138
Pearlite, 245
Pentaerythritol, 85
Petroleum, 117
Phenosafranine, 142
Pholas, 191
Phonofilm, 162
Phosphors, 168
Phosphorescence, 166
Photion lamp, 162
Photoblepharon, 188
— catalysis, 77
Photochemical laws, 4, 5
— mechanisms, 11
— reactions, 70
Photo-conductivity, 133
Photo-electric cells, 161
— effect, 108, 133, 158, 159, 174
Photogenic cells, 188
Photography, 125
Photogravure, 153
Photo-halides, 127
Photo-polymerisation, 92
Photostationary state, 86
Photo-sterilisation, 195
Photosynthesis, 77, 80, 83, 88
Photo-voltaic cells, 163
Phthaleins, 139
Physical development, 147
Phytosterol, 218
Pigmentation, 205
Pigments, 39
Pinachrome, 139
Pinacol, 101
Pinacyanol, 140
Pinaverdol, 139
Pintsch gas, 19
Piperidine, 103
Pitchblende, 180
Platinotype, 157
Pointolite lamp, 111
Polarised light, 159
Polymerisation, 254
Positive, 149
Potassium nitrate, 57
— nitrite, 57
— permanganate, 62
— tellurocyanide, 136
Powder method, 236
Predissociation, 12
Printing, 151
— paper, 137
Prizma process, 156
Propionanilide, 101
Propionic acid, 120
Protection, ultra-violet, 186
—, X-rays, 265
Proteins, 193
Provitamin-D, 212
Pumpkin-seed oil, 219
Pyridine, 103
Pyrrol, 101

Quanta, 159
Quantum efficiency, 8
Quartz, fused, 87

Quinine bisulphate, 167
Quinoline red, 139

Radiation hypothesis, 5
Radium paint, 179
— preparation, 181
—, price of, 182
Ramie, 254
Rape-seed oil, 219
Rare earths, 262
Rayon, 254
Recalescence, 241
Reflexion, 22
Relief printing, 151
Rhenium, 263
Rhodopsin, 187
Rice-meal oil, 219
Rickets, 205
Ringworm, 259
Ripening, 146
Röntgen rays, 231
Rotating crystal, 236
Rubber, action of light on, 106
—, crystal structure, 245
—, stretched, 256

Safranol, 143
Safranone, 144
Schumann plates, 144
Schwarzschild constant, 150
Selenium cells, 53, 158
Semicarbazones, 103
Sensitisers, 139
Sensitivity, 129, 131
Sesamé oil, 22
Shea butter, 219
Sheringham lamp, 42
Silent electric discharge, 74, 123
Sillimanite, 250
Siloxen, 193
Silver body, 131
— choloride, 126
— citrate, 53, 126
— colloid, 127
— germ, 127
— halides, 130
— sub-halides, 126, 129
Skin, 209, 223
Smokes, 267
Sodium arsenite, 134
— chloride, 240
— thiosulphate, 136
Spectra, absorption, 11, 162, 271
—, carbon dioxide, 79
—, chlorine, 122
—, cholesterol, 210
—, ergosterol, 213
—, eye media, 187
—, hydrogen peroxide, 71, 72, 73
—, vegetable oils, 218
Spectral sensitivity, 137
Spectrometer, X-ray, 233
Spectrum, sunlight, distribution of, 15
Spinel, 46
Starch, 96
Sterilisation, 195
Stilbene, 93
Stimulative rays, 202
Sub-halide, 129
Sucrose, 96
Sugars, 96, 98
Sunlight, 15, 16, 17, 53
Surface ractions, 82, 86
Sycosis, 259

Tellurium compounds, 136
Tetrabrom-fluorescein, 139
Tetrachloroethane, 120
Tetraiodo-fluorescein, 139
Thallium chloride, 129
Thalofide cell, 158
Therapy, light, 202
—, radium, 185
—, X-ray, 258
Thiocarbamide, 136
Thiocarbanilide, 136
Thiocyanines, 141
Thio-*iso*cyanines, 141
Thio-semicarbazide, 136
Toluene, 97, 117
Transformation points, 2
Transmission, X-rays, 2
Transparency, 36
Trichlormethane, 9
Troostite, 245
Tuberculosis, surgical, 2
Tungsten arc, 204

Unimolecular reactions,
Uranyl acetate, 64
— sulphate, 62
Urea, 95
Uroxameter, 62
Uviarc, 30

Vaccine, 198
Vanillin, 101
Vegetable oils, 218, 219
Vinyl compounds, 92, 93
Viscose, 254
Visible image, 133
Vision, 187
Visual purple, 187
Vitaglass, 61, 62, 106, 216
Vitamins, 206
Vitamin A, 200, 206
— D, 195, 205, 212

Voltol, 109
Volvox globator, 188
Vulcanisation, 106

Water, photochemistry of, 70
—, sterilisation of, 198, 200
Weathering tests, 107
Whale oil, 219
Wine, 200
Wood's light, 113
Wool fat, 219
Xanthophyll, 77
Xerophthalmia, 206

X-rays applications, 228
X-rays detection, 259
— dosage, 259
— flaws, 259
— new elements, 260
— photography, 145
— therapy, 258
— spectra, 262
— spectrometer, 234
— tubes, 228, 231

Yeast, 212
— fat, 219

Zinc phosphors, 171
— sulphide, 108

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